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CHEMICAL

AND

PHYSICAL RESEARCHES.

BY

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THE NUMERICAL RELATION BETWEEN THE ATOMIC WEIGHTS, WITH SOME THOUGHTS ON THE CLASSIFICATION OF THE CHEMICAL ELEMENTS.

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Numerical relations between the atomic weights of the chemical elements have been very frequently noticed by chemists. One of the fullest expositions of these relations was that given by M. Dumas of Paris, before the British Association for the Advancement of Science, at the meeting of 1851. This distinguished chemist at that time pointed out the fact, that many of the elements might be grouped in triads, in which the atomic weight of one was the arithmetical mean of those of the other two. Thus the atomic weight of Bromine is the mean between those of Chlorine and Iodine; that of Selenium is the mean between those of Sulphur and Tellurium; and that of Sodium, the mean between those of Lithium and Potassium. M. Dumas also spoke of the remarkable analogies between the properties of the members of these triads, comparing them with similar analogies observed in Organic Chemistry, and drew, as is well known, from these facts arguments to support the hypothesis of the compound nature of many of the now received elements. Similar views to those of Dumas have been advanced by other chemists.

The doctrine of triads is, however, as I hope to be able to show in the present memoir, a partial view of this subject, since these triads are only parts of series similar in all respects to the series of homologues of Organic Chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number. All the elements may be classified into six series, in each of which this number is different, and may be said to characterize its series. In the first it is nine, in the second eight,

in the third six, in the fourth five, in the fifth four, and in the last three. The discovery of this simple numerical relation, which includes all others that have ever been noticed, was the result of a classification of the chemical elements made for the purpose of exhibiting their analogies in the lecture room. A short notice of this classification will, therefore, make a natural introduction to the subject.

Every teacher of Chemistry must have felt the want of some system of classification like those which so greatly facilitate the acquisition of the natural-history sciences. In most elementary text-books on Chemistry, the elements are grouped together with little regard to their analogies. Oxygen, Hydrogen, and Nitrogen are usually placed first, and therefore together, although there are hardly to be found three elements more dissimilar; again, Phosphorus and Sulphur, which are not chemically allied, are frequently placed consecutively, while Arsenic, Antimony, and Bismuth, in spite of their close analogies with Phosphorus, are described in a different part of the book. This confusion, which arises in part from retaining the artificial classification of the elements into metals and metalloids, is a source of great difficulty to the learner, since it obliges him to retain in his memory a large number of apparently disconnected facts. In order to meet this difficulty, a classification of the elements into six groups, differing but slightly from that given in the table accompanying this memoir, was made. The object of the classification was simply to facilitate the acquisition of Chemistry, by bringing together such elements as were allied in their chemical relations considered collectively. As the classification has been in use for some time in the courses of lectures on Chemistry given in Harvard University, I have had an opportunity for observing its value in teaching, and cannot but feel that the object for which it was made has been in a great measure attained. The series which is headed The Six Series will illustrate the advantage gained from the classification in a course of lectures, the elements which compose it being among those especially dwelt upon in lectures to medical students, and, generally, very widely separated in a text-book on the science. As Chemistry is usually taught, the properties of the members of this series, Nitrogen, Phosphorus, Arsenic, and Antimony, as well as the composition and properties of their compounds, make up a large body of isolated facts, which, though without any assistance for his memory, the student is expected to retain. Certainly it cannot be won-

dered at, that he finds this a difficult task. The difficulty can, however, be in a great measure removed, if, after he has been taught that Nitrogen forms two important acids with Oxygen, NO_3 and NO_5, that it unites with Sulphur and Chlorine to form NS_3 and NCl_3, and also with three equivalents of Hydrogen to form NH_3, he is also told that, if in these symbols of the Nitrogen compounds he replaces N by P, As, or Sb, he will obtain symbols of similar compounds of Phosphorus, Arsenic, and Antimony; for he thus learns, once for all, the mode of combination of all four elements, so that when he comes to study the properties, in turn, of Phosphorus, Arsenic, and Antimony, he has not to learn with each an entirely new set of facts, but finds the same repeated with only a few variations. Moreover, these very variations he will learn to predict, if he is shown that the elements are arranged in the series according to the strength of their electro-negative properties, or in other words, that their affinities for Oxygen, Chlorine, Sulphur, etc. increase, while those for Hydrogen decrease, as we descend. He will then readily see why it is that, though Nitrogen forms NO_3 and NO_5, it forms only NCl_3 and NS_3, and that this reason is correct he will be pleased to find confirmed when he learns that Phosphorus, which is more electro-positive than Nitrogen, and has, therefore, a stronger affinity both for Chlorine and Sulphur, forms not only PCl_3 and PS_3, but also PCl_5 and PS_5. Again, he will not be surprised, after seeing the affinity of the elements for Hydrogen growing constantly weaker as he descends in the series, to learn that a compound of Bismuth and Hydrogen is not certainly known. Should he inquire why, though NH_3 has basic properties, PH_3, AsH_3, and SbH_3 have not, he can be shown that the loss of basic properties passing from NH_3 to PH_3 corresponds to a decrease in the strength in of the affinity between the elements, and that if in PH_3, SbH_3, or AsH_3, atoms of Methyle, Ethyle, or other organic radicals analogous to Hydrogen, are substituted for the Hydrogen atoms, and more stable compounds thus obtained, strong bases are the result. The other series would afford similar illustrations, and, from my own experience, I am confident that no teacher who will once use the classification of the elements here proposed, or one similar to it, will ever think of attempting to teach Chemistry without its aid.

Classifications of the elements, more or less complete, have been given by many authors; but the fact that no one has been generally received, is sufficient to prove that they are all liable to

objections, and would, indeed, also seem to show that a strictly scientific classification is hardly possible in the present state of the science. The difficulty with most of the classifications is, undoubtedly, that they are too one-sided, based upon one set of properties to the exclusion of others, and often on seeming, rather than real, resemblances. This is the difficulty with the old classification into metals and metalloids, which separated Phosphorus and Arsenic, Sulphur and Selenium, because Arsenic and Selenium have a metallic lustre, while Phosphorus and Sulphur have not, though there could hardly be found another point of difference. For a zoölogist to separate the ostrich from the class of birds because it cannot fly would not be more absurd, than it is for a chemist to separate two essentially allied elements, because one has a metallic lustre and the other has not. Yet it is surprising to see how persistently this classification is retained in every elementary work on the science; and if it is sometimes so far modified as to transfer elements analogous to Selenium and Arsenic to the class of metalloids, this is only acknowledging the worthlessness of the principle, without being willing to abandon it. If there were any fundamental property common to all the elements, the law of whose variation was known, this might serve as the basis of a correct classification. Chemistry, however, does not as yet present us with such a property, and we must, therefore, here, as in other sciences, base our classification on general analogies. The most fundamental of all chemical properties is, undoubtedly, crystalline form, but a classification of the elements based solely on the principles of isomorphism is defective in the same way as it is in mineralogy. It brings together, undoubtedly, allied elements, but it also groups with them those which resemble each other only in their crystalline form. The mode of combining seems to be also a fundamental property; but, like crystalline form, it would bring together in some instances elements differing very widely in their chemical properties. A classification of the elements which shall exhibit their natural affinities must obviously pay regard to both of these properties. It must at the same time seek to group together isomorphous elements, and those which form analogous compounds. Moreover, in such a classification other less fundamental properties must not be disregarded. There are many properties both physical and chemical, which, although they cannot be exactly measured, and are oftentimes difficult to define (such properties as those by which a chemist recognizes a

familiar substance, or a mineralogist a familiar mineral), and which on account of their indefinite character cannot be used as a basis of classification, may, nevertheless, render important aid in tracing out analogies. Judging from such properties as these, chemists are generally agreed in grouping together Carbon, Boron, and Silicon, although they cannot be proved to be isomorphous, and are not generally thought to form similar compounds.

It is, however, much easier to point out what a classification should be, than to make one which shall fulfil the required conditions. Indeed, as has been already said, past experience would seem to show that a perfect scientific classification of the elements is hardly possible in the present state of Chemistry. At best, the task is attended with great difficulties, and it cannot be expected that these should be surmounted at once. The classification which is offered in this memoir will, undoubtedly, be found to contain many defects. If, however, it is but one step in advance of those which have preceded it, it will be of value to the science. It was originally made, as has already been said, simply for the purpose of teaching, and never would have been published had it not led to the discovery of the numerical relation between the atomic weights.

On turning to the table which accompanies this memoir, it will be seen that the elements have been grouped into six series. These correspond entirely to the series of homologues of Organic Chemistry. In the group of volatile acids homologues of Formic Acid, for example, we have a series of compounds yielding similar derivatives, and producing similar reactions, and many of whose properties, such as boiling and melting points, specific gravity, etc., vary as we descend in the series according to a determinate law. From Formic Acid, a highly limpid, volatile, and corrosive fluid, the acids become less and less volatile, less and less fluid, less and less corrosive; first oily, then fat-like, and finally hard, brittle solids, like wax. As is well known, the composition of these acids varies in the same way, and the variation follows a regular law, so that by means of a general symbol we can express the composition of the class. This symbol for the volatile acids may be written $(C_2H)O_3$, $HO + n(C_2H_2)$.

This description of the well-known series of the volatile acids, applies, word for word, *nominibus mutatis*, to each of the six series of chemical elements. The elements of any one series form similar compounds and produce similar reactions: moreover, they re-

semble each other in another respect in which the members of the organic series do not. Their crystalline forms are the same, or, in other words, they are isomorphous. Although this may be true of the volatile acids, yet it cannot be proved in the present state of our knowledge. Still further, many of their properties vary in a regular manner as we descend in the series. In one case, at least, the law of the variation is known, and can be expressed algebraically, though in most instances it cannot be determined. Finally, as one general symbol will express the composition of a whole organic series, so a simple algebraic formula will express the atomic weight, or, if you may be pleased so to term it, the constitution of a series of elements.

These points may be illustrated with any of the series in the table; with the first, for example, which consists of Oxygen, Fluorine, Cyanogen, Chlorine, Bromine, and Iodine. All these elements form similar compounds, as will be seen by inspecting the symbols of their compounds given at the right hand of the list of names, where the similar or homologous compounds are arranged in upright columns. Moreover, they are all isomorphous, as may be seen by referring to the left-hand side of the list, where the similar compounds in each upright series are isomorphous, the numbers at the heads of the columns indicating the systems of crystallization, as is described in the explanation accompanying the table. That the properties of these elements vary as we descend can be easily shown. Oxygen is a permanent gas, as is also Fluorine. Cyanogen is a gas, but may be condensed to a liquid. Chlorine, a gas also, can be condensed more easily than Cyanogen. Bromine is a fluid at the ordinary temperature; and, finally, Iodine is a solid. Moreover, starting from Cyanogen, the solubility of these elements in water decreases as we descend in the series; and, again, the specific gravity of their vapors follows the inverse order of progression, gradually increasing from Oxygen down. The atomic weights vary in the same order, and admit of a general expression, which is $8+n9$, or, in other words, the differences between the atomic weights of these elements are always a multiple of nine. This general formula may be said to represent the constitution of these elements, in the same way that the symbol $(C_2H)O_3$, $HO + n(C_2H_2)$ represents the composition of the volatile acids before mentioned. In the place of $(C_2H)O_3$, HO we have $8 = O =$ the weight of one atom of Oxygen, and in the place of C_2H_2 we have nine. What it is that weighs nine (for it must be

remembered that those numbers are weights) we cannot at present say, but it is not impossible that this will be hereafter discovered. In order to bring the general symbol of the volatile acids into exact comparison with that of the Nine Series, we must reduce the symbols to weights, when the two formulæ become

$$46 + n14, \quad \text{where } 46 = (C\,H)O_3,\,HO \quad \text{and } 14 = C_2H_2;$$
$$\text{and } 8 + n\,9, \quad \text{where } 8 = O \quad \text{and } 9 = x.$$

The numbers 46 and 14 are known to represent the weights of aggregations of atoms. The number 8 represents the weight of one Oxygen atom, but we cannot as yet say what the 9 represents. After this comparison, it does not seem bold theorizing to suppose that the atoms of the members of this series are formed of an atom of Oxygen as a nucleus, to which have been added one or more groups of atoms, the weight of which equals nine, or perhaps one or more single atoms each weighing nine, to which the corresponding element has not yet been discovered. As it will be convenient to have names to denote the two terms of the formulæ which represent the constitution of the different series, we will call the first term, in accordance with this theory, the nucleus, and the number in the second term multiplied by *n* the common difference of the series.

From what has been said, it will be seen that the idea of the classification is that of the organic series. It is in this that the classification differs from those which have preceded it. Other authors, in grouping together the elements according to the principles of isomorphism, have obtained groups very similar to those here presented. Indeed, this could not be otherwise, since, as has been already said, the members of each series are isomorphous, while as a general rule, to which, however, there are many exceptions, no isomorphism can be established between members of different series. These groups, however, have been merely groups of isomorphous elements, and not series of homologues like those in which the elements are here classed.

These general remarks will suffice to indicate the principles upon which the classification has been made, and the character of the numerical relation between the atomic weights which has been established. The details of the classification can be best studied by referring to the table, so that it will be only necessary to speak of those points which are of special interest, or which may require explanation, or in regard to which there may be doubt. The

series I have named from their common differences. The first I have called the Nine Series, the second the Eight Series, etc. Let us examine the doubtful points in each, commencing with the first.

The last five members of the Eight Series are connected by so many analogies, that they have been invariably grouped together in the elementary books. There can be no doubt, therefore, in regard to the propriety of placing them in the same series, on the ground of general analogies. Fluorine, it is true, presents some striking points of difference from the rest. Fluoride of Calcium is almost insoluble in water, while the Chloride, Bromide, and Iodide of Calcium are all very soluble. We must, however, remember that we have to do with series, and must not therefore expect to find close resemblances except between adjacent members. If, then, we consider that Oxygen is one of the series, and that Fluorine stands but one step removed from Oxygen, while it is two steps removed from Chlorine, the discrepancy in a measure vanishes, for Lime CaO is but slightly soluble in water. Nevertheless, the difficulty does not entirely disappear, for CaFl is much less soluble than CaO, although it should be more soluble judging from the law of the series and the fact that CaCl is so much more soluble than CaFl.

The solubility of a series of homologous elements or compounds in water may be regarded as a function of one or more variables. In the case of elements there may be but one variable, but it is easy to see that in the case of compounds there must be several. One of these variables is probably the same which determines the common difference of the series to which the elements or compounds belong (it will be hereafter shown that the atomic weights of the homologous compounds are related in the same way as those of the elements); the other variables are perhaps the atomic forces which determine the hardness, density, etc., of the solid. We may, therefore, with justice, compare the relative solubilities of a series of homologues to a curve which should be the same function of the same variables; and what mathematics teaches we ought reasonably to expect in the case of this curve, we ought to expect also in the variations of solubility of these substances. Now, every mathematician is familiar with the remarkably rapid changes which a curve undergoes that is a function of several variables, and we cannot be surprised that similarly rapid changes should be observed in the solubility of homologous substances in passing

from one to the next in the series. In the curve which corresponds to the relative solubility of CaO, CaFl, CaCy, CaCl, CaBr, and CaI, it would seem that at CaFl there is a singular point where the curve, after rising for some distance above the axis, bends down again towards it. Several of the other series of compounds of these elements present similar anomalies; for example, KO, KFl, KCy, KCl, KBr, and KI. Here the solubility diminishes until we come to KCl, which is less soluble than KCy; then it increases to the last. Here, of course, the singular point is at KCl. With the corresponding compounds of sodium, the solubility diminishes to NaFl, which is the least soluble of the series, and then increases constantly to the end.

These facts at least seem to show that apparent variations from the law of series in properties, which evidently are unknown functions of several variables, should not be allowed to outweigh strong analogies, and certainly the analogies between Fluorine and the other haloids are very marked. Fluorine itself possesses properties such as we should expect to find in a member of the series above Chlorine. The strong and active affinities of Fluorine might be indeed predicted, after seeing the rapid increase both in the strength and activity of the affinities in passing from Iodine to Chlorine. In passing from Bromine to Chlorine, we pass from a liquid to a gas, permanent under any natural conditions; and we should expect, therefore, in rising still higher in the series, to find in Fluorine a gas less easily reduced to a liquid than Chlorine. Now although, on account of its remarkably active affinities, this fact cannot be demonstrated on the gas itself, it can, nevertheless, be inferred with perfect certainty from its compounds. Finally, the isomorphism of Fluorine and the other haloids may be urged as indicating close analogy. From these considerations, I cannot but think that those chemists who have questioned the propriety of classing Fluorine with the other haloids will, on reviewing the facts, and regarding the haloids in the light of a series, and not simply as a group of elements possessing certain general properties, be led to change their opinion.

Cyanogen, though a compound radical, has been classed with the other haloids, not only from its atomic weight, but also from its other analogies. Its properties are in most cases those which we should expect from an element occupying its position in the series; but in others it presents remarkable variations, owing probably to the fact that it contains a radical which is easily decomposed. As well known, it is perfectly isomorphous with Chlorine.

The propriety of classing Oxygen in this series seems to be placed beyond doubt by the discovery of Ozone, which, though it does not seem to possess such energy as we should expect in an element higher in the series than Fluorine, may, nevertheless, be found to fulfil all anticipations should it ever be obtained in a perfectly unmixed condition. The isomorphism of Oxygen with Chlorine, and therefore with the other håloids, seems sufficiently established by the determination both of Proust and Mitscherlich of the tetrahedral form of Cu_2Cl. It must, however, be admitted that Oxygen presents as strong analogies with Sulphur as it does with Chlorine; and since, not only from its analogies, but also from its atomic weight, it appears to be the nucleus in all the first three series, I have placed it at the head of each. It may be mentioned here, that in all cases the fact that the atomic weight of an element is included in the general formula of a series, is an argument for classifying it in that series, if the relation between the atomic weights pointed out in this memoir is admitted to be a law of nature; but as I wish to show that the relation is not that of a mere accidental group of numbers, but is connected with the most fundamental properties of the elements, and has therefore the claims of a law, I have endeavored to establish the correctness of the classification which conforms to the law, and, indeed, suggested the law on other grounds.

The atomic weights of the numbers of the Nine Series, as determined by experiment, present greater deviations from the numerical law already explained, than are to be found in any of the others. The weights which would exactly conform to the general formula $8 + n\,9$ are given in the column of the table headed Theoretical, while in the next column at the right are given the weights of experiment. These for the most part (in this as well as in the other series) have been taken from the table of Atomic Weights given in the last volume of Liebig and Kopp's *Jahresbericht* (for 1852), which was supposed to give the most accurate and latest results. In the few cases in which the numbers have not been taken from this table, the initial letter of the name of the observer has been annexed. It will be seen, on comparing the two columns, that the greatest deviation from the law is in the case of Fluorine, if we consider the care which was taken both by Berzelius and Louyet in the determination of the atomic weight of this element. It may, however, be remarked, that, as the processes used by both experimenters were essentially identical, any

hidden constant source of error would produce the same effect on both results; so that the atomic weight of Fluorine cannot be regarded as yet as absolutely fixed. Nevertheless, it is not possible that so great a difference between the true and observed weights as two units could have escaped detection in the numberless analyses which have been made, by the most experienced chemists, of the Fluorine compounds. It must, therefore, be admitted, and not only in the case of Fluorine, but also in other instances, that there are deviations from the law; but these deviations are not greater than those from similar numerical laws in astronomy and other sciences, and indeed, judging from the analogy of these sciences, ought to be expected.

Those who are not familiar with the amounts of probable error in the determination of the different atomic weights would judge, on comparing together the columns of theoretical and observed values, that the deviations from the law were much greater than they are in reality. It should, therefore, be stated, that, in by far the larger number of instances, the deviations are within the limit of possible errors in the determinations, leaving only a few exceptional cases to be accounted for. It must be remembered that, other things being equal, the amount of probable error is the greater the greater the atomic weight, so that a difference of 1.9 in the case of Iodine is not a greater actual deviation from the law than only 0.5 in the case of Chlorine. Indeed, it is very possible that on more accurate determinations the atomic weight of Iodine will be found to correspond to the law, which cannot be expected of that of Chlorine. It is well known that many of the larger atomic weights, especially those of the rarer elements, cannot be regarded as fixed within several units.

I have calculated, as well as the data I have would permit, the amount of probable error in the determinations of many of the atomic weights, and by comparing together the results from different processes, and by different experimenters, I have endeavored to detect the existence of constant errors, which seem to be the great errors in all these determinations, those accidental errors which are made in the repetitions of the same process by equally careful experimenters being comparatively insignificant. The results of this investigation will be published in a subsequent memoir. It is sufficient for the present purpose to state, that, while they show that, in the greater number of cases, the apparent variations from the law are within the limit of probable error,

there are yet several instances where, after allowing for all possible errors of observation, there is a residual difference. I do not therefore look alone to more accurate observations for a confirmation of the law, but, regarding the variations as ascertained facts, hope that future discovery will reveal the cause. Whether the variations will be found to be a secondary result of the very cause which has determined the distribution of the atomic weights according to a numerical law, as the perturbations in astronomy are a necessary consequence of the very law they seemed at first to invalidate, or whether they are due to independent causes, can of course, for the present, be only a matter of speculation. There are, however, facts which seem to indicate that the variations are not matters of chance, but correspond to variations in the properties of the elements.

From the beautiful discovery of Professor Schönbein we have learnt that Oxygen has two allotropic modifications, and that besides its ordinary condition it is capable of assuming another highly active state, when its properties resemble those of Chlorine. Cyanogen is only known in a quiescent state. The other haloids, Fluorine, Chlorine, Bromine, and Iodine, are only known in a highly active state. Now it will be seen on examining the table, that the atomic weights of the highly active elements, as determined by experiment, exceed slightly the theoretical numbers, and that where the affinities are the most intense, in Fluorine, the deviation is the greatest. A similar fact may be observed in the atomic weights of the members of the Six Series. Arsenic has been proved to be capable of existing in two allotropic modifications. In its ordinary state, it has a crystalline form belonging to the Rhombic System. In the other condition, in which it may be obtained by sublimation at a low temperature, it crystallizes in regular octahedrons. The other members of this series are probably isodimorphs with Arsenic. The ordinary condition of Phosphorus is its monometric modification, while the rhombic state seems to be the normal condition of Arsenic, Antimony, and Bismuth. Now the atomic weights of the last three are either equal to, or slightly exceed, the theoretical number, while that of the first fall short, perhaps even by a unit. Other facts, which also tend to show that the deviations are not matters of chance, may be found in the affiliations of the series. There are some elements which seem to be most remarkably double-faced, having certain properties which connect them closely with one series, and at the

same time others which unite them nearly as closely to another. In such cases we find that the atomic weight either falls naturally into both series, or, not corresponding exactly with the theoretical number of the series to which the element properly belongs, it inclines towards that of the other, and sometimes equals it. Such is the case with Chromium, Manganese, and Gold, as will be seen by referring to the affiliations at the bottom of the Nine Series. These various facts force upon me the conviction, that this relation between the atomic weights is not a matter of chance, but that it was a part of the grand plan of the Framer of the universe, and that in the very deviations from the law there will hereafter be found fresh evidence of the wisdom and forethought of its Divine Author.

The general formulæ for the Eight Series are $8 + n\,8$ and $4 + n\,8$. The two nuclei correspond to two different sets of elements, or sub-series, one consisting of Oxygen, Sulphur, Selenium, and Tellurium, the other of Molybdenum, Vanadium, Tungsten, and Tantalum. The atomic weights of the first are all equal to $8 + n\,8$; those of the second to $4 + n\,8$. The sub-series exhibit marked analogies, as well as certain differences. They resemble each other chiefly in that the members of both form analogous acids with Oxygen, while they differ in that, though the members of the first sub-series form compounds with Hydrogen, those of the second do not. The isomorphism of the members of each sub-series among themselves, with the exception of Vanadium, is complete; but there seems to be no proof of any isomorphism between the sub-series. Johnston attempted to establish the isomorphism of Chromic and Molybdic Acids from the red variety of Molybdate of Lead from Rezbanya, which he supposed to be a Chromate; but the fact has been disproved by G. Rose, who has shown that the supposed Chromate is a Molybdate mixed with a small amount only of Chromate. There seems, nevertheless, to be some reason for believing that Chromic Acid may replace Molybdic Acid to a certain extent. If this is proved, it establishes another link of connection between the members of the two sub-series, since Chromic Acid is isomorphous with Sulphuric Acid. For the present, however, we must regard them as sub-series, related, but distinct, the second being in a measure supplementary to the first. They are distinguished in the table by printing the names of the second sub-series a little to the right of those of the first, and the fact that their atomic weights are intermediate to those of the first I have indi-

cated to the eye by giving to the names also an intermediate position.

The analogies between Oxygen and Sulphur are so numerous, that, were we to place Oxygen in but one series, we should place it in this. HO and HS, HO_2 and HS_2, resemble each other very closely, as do also the Oxygen salts the corresponding Sulphur salts. Moreover, there can be no doubt in regard to the isomorphism of the two elements, since it has been established upon the authority both of Mitscherlich and Becquerel, and from two different compounds. The only doubtful case in the series was that of Vanadium, which in some of its properties resembles Arsenic more closely than it does Molybdenum. The reasons for giving it the place which it occupies were the facts that its acids correspond to those of Molybdenum, and that it forms remarkably highly colored oxides which are repeated also in Molybdenum. It is true that the properties of the element itself are not those we should expect from the position which it occupies in our table; yet, if it were placed in the Six Series, it would fall between Phosphorus and Arsenic, which on the whole it resembles less than it does Molybdenum, for although it is combustible, yet neither it nor its oxides are volatile. I consider it, therefore, as a member of the Eight Series, but affiliating very closely with the Six. Its atomic weight favors this hypothesis. Vanadate of Lead has been considered isomorphous with the Phosphate; but as this isomorphism does not rest on any measurement of angles, and as, moreover, the received symbols of the two minerals, Vandinite and Pyromorphite, on whose crystalline forms the isomorphism was determined, show a very different constitution, I have not given much weight to this fact.* The observed atomic weights of the numbers of this series are almost precisely the same as the theoretical members, and, with the exception, perhaps, of Molybdenum, there appears to be no instance in which the difference is greater than the amount of possible error.

The members of the Six Group form a well-characterized family, so that, with the exception of Oxygen, there can be no doubt in regard to the justice of classifying them together, and any discrepancies will disappear on considering the group in the light of a series. They form acids containing three and five atoms of Oxygen which are completely homologous, and make two series parallel to that of the elements. They form also a remarkable series of compounds with three atoms of Hydrogen. The idea which has been advanced by some authors, that NH_3 is the Nitride of Hydrogen,

* See G. Rose's Mineral System.

while PH_3 is the Hyduret of Phosphorus, or, in other words, that Hydrogen is electro-positive with reference to Nitrogen and electro-negative with reference to Phosphorus and those lower in the series, does not seem to me correct, since the remarkable bases which may be formed from PH_3, AsH_3, SbH_3, and BiH_3, by replacing the Hydrogen atoms by organic radicals, seem to indicate that they have the same type as NH_3, and are therefore homologues of it.

The isomorphism of the four lower members of the series is perfect. It has been shown in the table, both by the crystalline forms of the elements themselves, as well as by those of their compounds. In the other series, wherever it was possible, the same double proof has been given. The doubt expressed by G. Rose in regard to the dimorphism of Arsenic, as I hope to be able to show in a paper soon to be published, has been removed. In one state Arsenic crystallizes in perfect octahedrons of the regular system, and is therefore isomorphous, not only with Antimony and Bismuth, but also, in its allotropic state, with Phosphorus. Isomorphism, as is well known, is not absolute, except in forms of the regular system. The rhombic angles of the crystals of Arsenic, Antimony, and Bismuth are respectively 85° 41′, 87° 35′, 87° 40′, and therefore conform to the general rule. It will be observed that the angle varies constantly in the same way as we descend in the series. Now, although these few instances do not afford sufficient ground for any general conclusion, yet they show that similar variations are possible in the other systems, and therefore that we cannot be expected to establish isomorphism in any case except between nearly consecutive members.

The atomic weights of the members of this series, with the exception of Phosphorus, do not present any important deviations from the theoretical numbers, taking into account always, of course, the amount of possible error. The deviation in the case of Phosphorus has already been noticed. Oxygen, it must be admitted, is not connected with the series from any similarity of properties, though the Phosphides, Arsenides, and Antimonides present certain analogies with the Oxides. As has already been said, Oxygen was placed at the head of this, as well as of the last two series, because its atomic weight seemed to be the nucleus of all three.

The Five Series is the shortest of all, consisting of only three members, Carbon, Boron, and Silicon. Of these, the last two are as closely allied as are any two members of the other series, Silicon

having precisely the properties we should expect in a homologue of Boron, which was lower in the series; and the same is also true of their compounds. The analogies, however, between these two elements and Carbon are by no means so close, for not only Carbon cannot be proved to be isomorphous with them, but it does not form similar compounds. Carbonic Acid, it is true, presents some points of resemblance to Boracic and Silicic Acids; like them it unites in a large variety of proportions with bases, its alkaline salts give a basic reaction, etc.; but according to the generally received opinion, its symbol is CO_2, while those of Boron and Silicon are BO_3 and SiO_3. In its uncombined state, however, Carbon resembles Boron and Silicon, not only in its outward properties, but also in its action before the blowpipe. Two of the allotropic states of Carbon, Graphite and Charcoal are probably repeated in Boron, and are known to be in Silicon. The principle of exclusion would also seem to place Carbon in this series, for it certainly presents no analogies with the members of any other. The correspondence of the atomic weights of the members of this series to the law is remarkably close.

The Four Series is by far the largest of all, including the greater number of what are generally known as the heavy metals. The members of the series resemble each other in the following respects. First, they are isomorphous; for although each member cannot be directly proved to be isomorphous with every other, yet isomorphism can be established between consecutive members, which, as has before been said, is all that can be expected. Second, the members of this series all form, by uniting with Oxygen, either Protoxides or Sesquioxides, or both, which, as a general rule, are strong bases. Third, these Oxides are either insoluble, or nearly insoluble, in water. And finally, the elements of the series have all those physical properties which are known as metallic properties.

This series may be naturally divided into two sub-series. The first contains those elements whose protoxide bases are their characteristic compounds, and which do not form acids with Oxygen. The second contains those elements whose characteristic compounds are their sesquibases. They generally unite with two or more equivalents of Oxygen, and form acids. These sub-series are distinguished in the table in the same way as those of the Six Series. Corresponding to these sub-series we have two sets of atomic weights, each having the same common difference, but

differing in their starting-point or nucleus. The first set is expressed by the formula $4 + n\,4$, the second by $2 + n\,4$.

The sub-series affiliate with each other in a most remarkable manner. Manganese, for example, not only forms a strong protoxide base, but also unites with a larger amount of Oxygen, forming both a sesquibase and acids. Its atomic weight places it in the first group, and it has therefore been classed there, although by its properties it is equally allied to the second. Cobalt and Nickel certainly resemble much more closely the members of the first than of the second sub-series, although their atomic weights place them in the second. With this exception, the subdivision of the series which the atomic weights require does not differ from that suggested by the properties of the elements. The members of this series may of course be still further subdivided into groups according to their special properties, as they are in all works on Chemistry. They are placed together here because the atomic weights form but one numerical series.

The isomorphism of the members of this series will be found well established with the limitations before given. In order to establish the isomorphism of Cobalt and Nickel with Iron, the isomorphism of one atom of Arsenic with two atoms of Sulphur has been assumed. This is generally admitted; but if it is not, no one can doubt in regard to the isomorphism of these three metals, as they constantly replace each other. Glucinum, Zirconium, Lanthanum, Cerium, and Thorium cannot be shown to be isomorphous with the other metals by any of their compounds, but their oxides are known to replace the analogous oxides of the other metals. So also is Ruthenium known to replace Rhodium. There have been doubts expressed in regard to the existence of a monometric form of Zinc; but as we have established its isomorphism with the other members of the series, not only by its own crystalline form, but also by those of its compounds, the fact is of no importance to the present question.

The atomic weights of the members of this series, as determined by observation, very nearly correspond with the theoretical numbers, which is the more remarkable, as the limit of error in the determination of the atomic weights of the greater number, especially of the rarer metals, is quite wide.

The Three (and last) Series is composed of Hydrogen and the metals of the alkalies. The analogies between Lithium, Sodium, and Potassium are very close, as is well known, and there can be

no doubt in regard to the propriety of classing them together. It may be said, however, in regard to Hydrogen, that it resembles as closely some of the metals of the Four Series as it does those of the alkalies. Though this cannot be denied, yet the fact that the atomic weight of Hydrogen is the nucleus of the series, and the great solubility of the alkalies in water, may be urged as reasons for placing it at the head of the Three Series.

The isomorphism of Lithium, Sodium, and Potassium is fully established; but I can find no data which prove Hydrogen isomorphous either with them or with the metals of the other group.

The unit of the atomic weights which has been used thus far throughout the table, is the double atom of Hydrogen; but the nucleus of the Three Series is the weight of the single atom, so that the unit in this series is one half of the unit of the weights in all the other series. This fact must be kept in mind in comparing the atomic weights of this with those of the other series. All the weights might have been made uniform by doubling them throughout; but as this would not have changed the relation, and would have been departing from the general custom, it was thought best to confine the doubling to the Three Series, into which alone Hydrogen enters. The general symbol of this series is $1 + n\,3$, where of course the unit is one half of that of the symbols at the head of the other series. The observed atomic weights will be found to correspond very closely with the theoretical numbers; indeed, the two coincide, except in the case of Potassium, where the difference is 0.6. This, however, it must be remembered, is 0.6 of the single Hydrogen atom. Compared with the double atom, as the weight of Potassium is generally given, the difference amounts to but 0.3.

One of the most remarkable points of the classification which has been now explained, is the affiliation of the series. We find in Chemistry, as in other sciences, that Nature seems to abhor abrupt transitions, and shades off her bounding lines. Many of the elements, while they manifestly belong to one series, have properties which ally them to another. Several examples of this have already been noticed. In such cases, we find invariably that there is a similar affiliation of the atomic weight. Of all the elements Chromium and Manganese are the most protean. Two atoms of these elements unite with seven atoms of Oxygen and form acids analogous to Perchloric Acid, and, as has already been shown, the weight of two atoms of either element falls into the

Nine Series. Moreover, one atom of Chromium or of Manganese unites with three atoms of Oxygen to form Chromic or Manganic Acid. Chromic Acid is a strong oxidizing agent, and resembles closely Nitrous Acid, and the atomic weight of Chromium falls into the Six Series just below that of Nitrogen. Manganic Acid, on the other hand, resembles Sulphuric Acid, with which it is isomorphous, and the atomic weight of Manganese would place it in the Eight Series. In like manner Osmium in many of its properties resembles Platinum and the other metals with which it is associated in nature; but, unlike them, it forms a very remarkable volatile acid, whose insupportable and suffocating odor as well as composition reminds one of the acids of the Nine Series, and its atomic weight seems to justify the apparent analogy. Gold likewise, though the noblest of metals, yet in some of its chemical relations resembles much more closely the members of the Nine than of the Four Series, and here again its accommodating atomic weight seems to account for its double-sided character. Several other examples of similar affiliations are given in the table, but do not need explanation.

In the description just concluded of the classification of the chemical elements, which is offered in this memoir, I have not entered into details, for to have done so would have been to write a trêatise on Chemistry. I have confined myself almost exclusively to general points, and only referred to those particulars which I thought might present doubts. I hope that I have been able to show, first, that the chemical elements may be classified in a few series similar to the series of homologues of Organic Chemistry; second, that in those series the properties of the elements follow a law of progression; and finally that the atomic weights vary according to a similar law, which may be expressed by a simple algebraic formula. As already intimated, I have endeavored to prove the correctness of the classification on general grounds, in order that it might appear that the simple numerical relation which has been discovered between the atomic weights is not a matter of chance, but is connected with the most fundamental properties of the elements. I might leave the subject at this point, but the existence of the law which I wish to establish will be proved more conclusively if it can be shown, not simply that the general properties of the members of each series vary in a regular manner, but also if in one or more cases the exact law of the variation can be pointed out.

There are but few properties of the elements which are subjects of measurement, and which therefore can be compared numerically. Such are the specific gravity in the three states of aggregation, the boiling and melting points, the capacity of heat, and a few others. It is easy to see that there are but few of these properties the law of whose variation in the series we could reasonably expect to discover in the present state of science. Most of them evidently depend upon molecular forces with which we are entirely unacquainted. Such in solids is undoubtedly the case with so simple and fundamental a property as specific gravity, and most, if not all, of the other properties of solids belong to the same category. It cannot therefore be expected that we should point out the laws by which these properties vary, although the remarkable investigations of Dana, Filhol, Kopp, Schröder, and others, on the relations between the density of substances and their atomic weights, and those of Kengott on the relation of hardness to atomic volume, give grounds for expecting that even they will before long be discovered. In liquids and gases, however, most of these molecular forces which produce the apparent irregularities in solids have less influence, as we should naturally expect, probably because the atoms are removed out of the sphere of their action. We may therefore hope, on comparing together the properties of the liquid or gaseous states of the elements in any series, to discover some numerical relation between them. Unfortunately, however, we have not sufficient data for making such a comparison except in the case of one property, the specific gravity. The boiling point, which would be a very valuable property for the purpose, is known only in a few instances.

That the specific gravity of the elements in their gaseous state varies in each series according to a numerical law, follows necessarily from what is already known. It is a well-known fact, that the specific gravities of the gaseous states of the elements divided by their atomic weights give quotients which are either equal, or which stand in a very simple relation to each other. For any series, as far as we have data, this quotient is the same for all the elements with only a few exceptions. That is $\frac{\text{Sp. Gr.}}{\text{At. W.}} = p$. But we have found that At. W. may be expressed in general by $a + nb$, and substituting this for At. W. in the above equation, it becomes $\frac{\text{Sp. Gr.}}{a + nb} = p$, or Sp. Gr. $= pa + npb$; so that $pa + npb$ is a general expression for the specific gravity of all

the elements of any series, in the same way that $a + n\,b$ is for the atomic weight. The value of p will differ according as the specific gravities used are referred to Hydrogen or Air. Below will be found tables which give the calculated and observed specific gravities of the elements of the Nine and Six Series referred to Hydrogen, which has been taken as the unit instead of Air, as we thus in great measure avoid fractions. In the Nine Series $p = 1$, so that the numbers representing the specific gravities are the same as those representing the atomic weights. In the Six Series it equals two, so that the numbers representing the specific gravities are in this series twice as large as those representing the atomic weights. When the specific gravity has not been observed, the calculated number only is given. The observed numbers are taken from the "Table of Specific Gravity of Gases and Vapors," in Graham's *Elements of Chemistry*, which is a very complete collection of all known data. For the other series, we have only occasional data, so that no complete tables of their specific gravities are possible.

THE NINE SERIES. $\frac{\text{Sp. Gr.}}{\text{At. W.}} = 1.$ Sp. Gr. $= 8 + n\,9$.			THE SIX SERIES. $\frac{\text{Sp. Gr.}}{\text{At. W.}} = 2.$ Sp. Gr. $= 16 + n\,12$.		
Names.	Specific Gravities.		Names.	Specific Gravities.	
	Theoret.	Observed.		Theoret.	Observed.
Oxygen	8	16	Oxygen	16	16
Fluorine	17	..	Nitrogen	28	14
Cyanogen	26	26	Phosphorus	64	64
Chlorine	35	35.5	Arsenic	148	150
Bromine	80	78	Antimony	256	..
Iodine	125	126	Bismuth	412	..

It is evident, then, that at least one property of the elements varies in the series according to an ascertained numerical law. But, it may be said, this proves nothing, for these specific gravities are connected so closely with the atomic weights that what is true of the one must be to the same extent true of the other. It must be remembered, however, that the specific gravities are a distinct set

of observed facts, and that the probability of a law is in exact proportion to the number of facts which accord with it. Moreover, the closeness of the connection is unimportant. Whether the value of p be expressed by a single digit, or by a complicated algebraic formula, is evidently a matter of indifference so far as the confirmation of the law is concerned.

I regret exceedingly that there are not sufficient data in the case of any of the other properties of the elements in the state of gas to allow comparison, as I feel confident that the law which governs their variation in the series might easily be discovered; but I look forward to the time when in the general formula $pa + npb$ the value of p shall be known, not only for the properties of the elements in their gaseous state, but for every property capable of numerical expression.

In this memoir I have confined myself entirely to the elements, but it is evident that the classification here offered, and the numerical law here explained, may be extended to all compounds. The elements of any one series, by combining, give rise to perfectly parallel series of homologous binaries, some of which are given in the table. The binaries of those series which have the greatest common difference are generally acids; and of those which have the smallest, they are generally bases. These acids and bases unite together and form series of homologous salts. As in Organic Chemistry, many of the series are very incomplete; but they are much more generally perfect than in that newer department of the science, and almost every day fills up some gap.

It will be seen, then, that not merely a plan has been given for classifying the elements, but one which will also embrace all inorganic compounds, and affiliate with the similar classification which has already been established in Organic Chemistry. We have not attempted to develop such a classification, since to do it would require a volume; nor is it necessary, as any one can develop it for himself.

That the atomic weights of the series of homologous compounds follow the same numerical law as those of the elements is easily shown. Take as an example the series of salts homologous with KO, NO_5, which may be expressed in general by KO, RO_5, where R is any member of the Six Series after Oxygen, and whose atomic weight, therefore, equals $8 + n 6$. The atomic weight of KO, RO_5 must be necessarily $39.5 + 48 + (8 + n 6)$, or $95.5 + n 6$. As this symbol differs from that of the Six Series only in the nucleus,

the atomic weights of the salts which are represented by it must progress by the same differences as those of the corresponding elements.

The properties of these series of homologous compounds will also be found to vary in a regular manner, and the law of the progression of the specific gravities in the gaseous state can be easily expressed algebraically, since in each series the quotient of the specific gravity divided by the atomic weight is a constant quantity. As an illustration we may take the series of binaries homologues of water given in the Nine Series of our table. It follows from what has been said, that the atomic weights of these compounds equals $9 + n\,9$. With each $\frac{\text{Sp. Gr.}}{9 + n\,9} = \frac{1}{2}$, therefore Sp. Gr. $= 4.5 + n\,4.5$. We give below a table of the observed or calculated specific gravities, not only of these compounds, but also of those homologues of NH_3 whose specific gravity has been observed.

HOMOLOGUES OF WATER. $\frac{\text{Sp. Gr.}}{\text{At. W.}} = \frac{1}{2}$. Sp. Gr. $= 4.5 + n\,4.5$.			HOMOLOGUES OF AMMONIA GAS. $\frac{\text{Sp. Gr.}}{\text{At. W.}} = \frac{1}{2}$. Sp. Gr. $= 5.5 + n\,3$.		
Symbols.	Specific Gravities.		Symbols.	Specific Gravities.	
	Theoret.	Observed.		Theoret.	Observed.
HO	4.5	9	NH_3	8.5	8.5
HFl	9	....	PH_3	17.25	17.5
HCl	18.5	18.5	AsH_3	39	38.5
HBr	40.5	39.5	....	....	....
HI	63	63.5	....	....	....

As the series of compounds give a greater scope for investigating the relations of properties than is presented by those of the elements, we may expect that these relations will be first discovered in the former, and to my conceptions Chemistry will then have become a perfect science, when all substances have been classed in series of homologues, and when we can make a table which shall contain, not only every known substance, but also every possible one, and when by means of a few general formulæ we shall be able to express all the properties of matter so that, when the series of a substance and its place in its series are given,

we shall be able to calculate, nay, predict, its properties with absolute certainty; and when our chemical treatises shall have been reduced to tables of homologues, and our laws comprised in a few algebraic formulæ, then the dreams of the ancient alchemist will be realized, for the problem of the transmutation of the elements will have been theoretically, if not practically, solved.

Explanation of the Table.

The formula at the head of each series is a general expression for the atomic weights of that series. The names of the series are derived from the "Common Differences," which are the numbers multiplied by *n* in the general formulæ. In the columns headed "Theoretical" are given the atomic weights calculated from these formulæ and the values of *n* given in the last columns at the right of each division of the table. In the columns headed "Observed" will be found the observed values of the same atomic weights. These have been taken from the table of atomic weights given in the last volume of Liebig and Kopp's *Jahresbericht* (for 1852), with the exception of those against which are placed the initials of the observers. The last were taken from Weber's *Atomgewichts Tabellen*. In some cases the atomic weight is taken at twice its received values, but it is then underlined. The compounds in any one column at the right of the names of the elements are homologous. In the same way, those in any one at the left are isomorphous. The numbers at the head of these last columns indicate crystalline systems as follows: 1. Monometric; 2. Dimetric; 3. Trimetric; 4. Monoclinic; 5. Triclinic; 6. Rhombic. The data from which the table was compiled were drawn from numerous sources, but especially from the following works: Gmelin's *Handbook of Chemistry*, Graham's *Elements of Chemistry*, Phillips's *Mineralogy* by Brooke and Miller, and Gustav Rose's *Krystallo-chemische Mineralsystem*. References have been given only in a few cases, to avoid crowding the tables. For authorities in other cases, the author would refer to the above-mentioned works.

CONTRIBUTIONS

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CONTENTS.

VIII.

ON A NEW MODE OF MANIPULATING HYDRIC SULPHIDE.

By Josiah P. Cooke, Jr.,

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Presented May 30th, 1876.

In chemical laboratories, where instruction in qualitative analysis is given to large numbers on the class system, the use of hydric sulphide gas as a reagent is attended with grave inconveniences. These evils can in great measure be avoided by substituting for the gas a solution of the reagent in water, saturated at the ordinary temperature and pressure of the air; when, as is well known, one volume of water dissolves about 3.4 volumes of the gas (measured at 15° C. and 76 cm.). Such a solution was for a long time used in the laboratory of Harvard College. It was prepared in a long series of two *litre* bottles connected by glass tubes in the usual way, and the solution was kept in the laboratory in a large tubulated glass flask, from which it was drawn by the students, as occasion required. This solution answers almost every purpose for which the reagent is used in the ordinary course of qualitative analysis, and the few conditions under which it does not give satisfactory results can be easily avoided. Moreover, in ease of application and promptness of effect it has all the advantages of a liquid reagent; and the only inconvenience its use involves is an occasional evaporation of a solution, which the dilution by the reagent may render necessary. Of course a solution of hydric sulphide is liable to oxidation, and soon becomes turbid in contact with the air; but this change can be easily avoided by fitting to the neck of the flask (in which the solution is kept), by means of a rubber stopper, a glass tube dipping under the liquid, and connecting this tube with one of the vents of illuminating gas in the laboratory.

For quantitative work, and for the preparation of chemical products, when considerable quantities of metallic sulphides must be precipitated, a solution of hydric sulphide, saturated under the ordinary pressure of

the air, is inconveniently dilute; and two years since we described a simple method by which a solution concentrated under pressure could easily be prepared with the ordinary laboratory appliances. A heavy glass bottle of about four litres' capacity served as a generator, and from this the gas passed through a wash-bottle into two other bottles of the same size and strength as the first. The intermediate bottle was three-fourths filled with water, while the last served simply as a gasholder. The connections were so arranged that the gas, after bubbling up through the water, was delivered at the top of the gasholder; and, by a tube uniting the bottom of the gasholder with the water-pipes of the laboratory, the interior of the apparatus could be submitted to the pressure of a column of water sixty feet high. The gasholder was also provided with an exit tube, which could be closed by a compression cock. The connecting tubes all passed through rubber stoppers which were firmly wired to the necks of the bottles, and the water-bottle was connected with its neighbors by two lengths of stout rubber hose so that the water could be shaken up with the gas without disturbing the rest of the apparatus. In order to saturate the water with hydric sulphide, a charge of ferrous sulphide sulphuric acid and water sufficient to yield at least three times the amount of gas theoretically required was placed in the generator, and, after the connections were made, the gas was allowed to stream through the apparatus until all the air was displaced. The exit tube of the last bottle was then closed, the water pressure turned on and the water-bottle frequently shaken, until absorption ceased, and the aqueduct water — at first forced by its pressure into the gasholder — was driven back into the pipes. Before dismounting the apparatus, the rubber connectors were all closed by compression cocks, and care was taken to vent the generator gradually. Moreover, the connectors of the water-bottle were so arranged that when the apparatus was dismounted a short piece of rubber hose was left attached to each orifice of the bottle, both of which were closed by compression cocks. To one of these a vent tube was subsequently attached, and by this the solution was drawn off at pleasure, as from a soda-water siphon.

This simple apparatus was constantly used by us for two years, and served an excellent purpose; but it was found that after the glass generators had been charged several times they were liable to burst under the same pressure which at first they had readily sustained. The same accident never happened to the other bottles. But of course, if the pressure is long continued, bottles of glass of the size named, however well made, would be liable to such an accident; and, if the

apparatus is to be remounted, it would be better to use a metallic vessel for the generator, and to cover the glass bottles with some kind of netting. The experience with the glass apparatus led us to seek to adapt to the same purpose some one of the various soda-water apparatuses which are greatly used in the United States for the production of effervescing drinks. After examining several of the patterns in the market, we selected for trial the one represented below, which is manufactured by the firm of John Matthews, of New York, at their establishment, — First Avenue, 26th and 27th Streets, — in that city. The apparatus was designed by them for preparing that overcharged aqueous solution of carbonic dioxide, which in the United States is familiarly called soda-water; but with a very slight modification it can be used with equal efficiency for the preparation of a similar solution of hydric sulphide. We have worked out the details of the process, which this new application involves, and publish them with the hope that the apparatus may be found of as great value in other laboratories

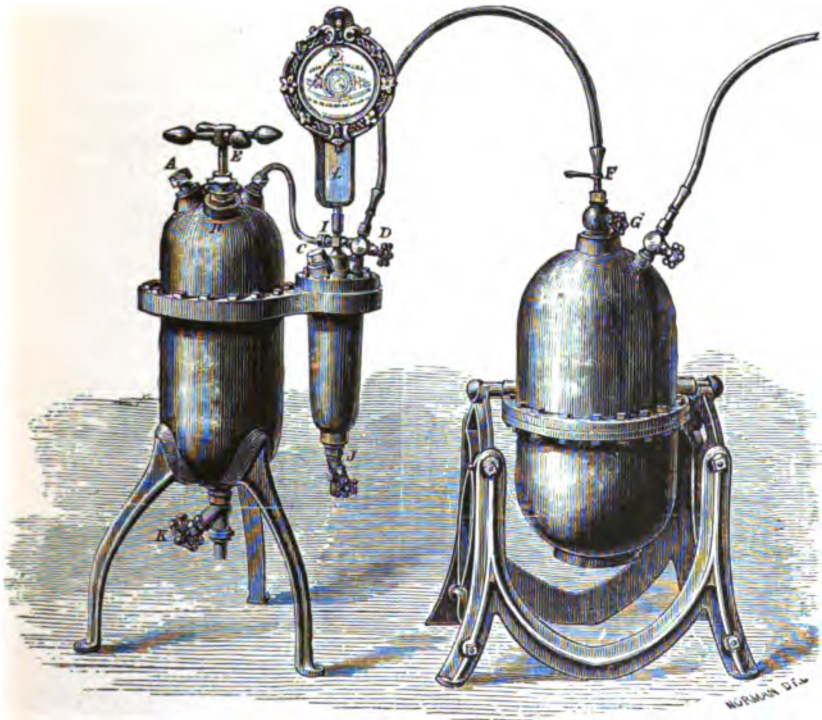


Fig. 1.

as in our own. The wood-cuts are taken from the catalogue of the firm, who have kindly loaned the blocks for this paper; and we would here express our obligations to them for their great courtesy and liberality during the whole course of our experiments.

The apparatus consists of two parts, the generator and the fountains; and in Fig. 1 the generator is represented connected by a rubber hose with one of the fountains, of which in practice we use three, connected in a line by similar lengths of rubber hose, like so many Woolf's bottles. In the figure, only the first of the line is represented, which is set on trunnions in a frame, in order to facilitate the agitation of the water and the gas. Only one of these frames, however, is required, to which the other fountains can readily be transferred. A section of the generator is represented in Fig. 2. It is made of cast iron, and in

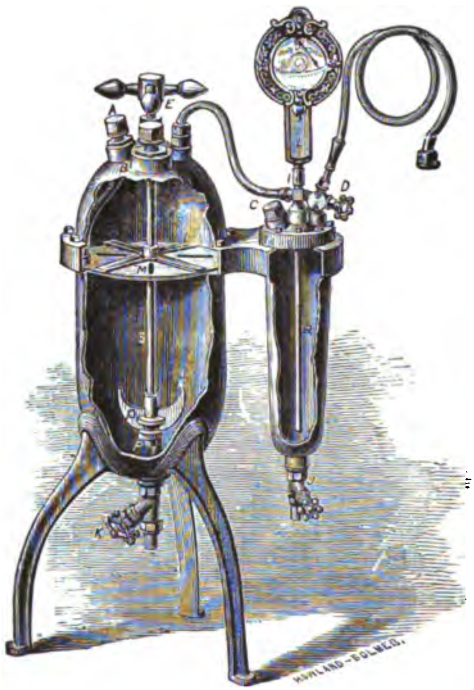


Fig. 2.

two parts (readily distinguished in the figure), which are firmly bolted together, so as to confine in its place the bell-metal plate M, which separates the upper from the lower chamber. In the lower chamber is placed dilute sulphuric acid, which is poured in through the bung A.

In the upper chamber, and resting on the plate, is placed coarsely powdered sulphide of iron, which is put in through the bung B. Through the plate M, and on two lines at right angles to each other, there are cut radial slits, ½ an inch wide, which are guarded by four iron arms. These arms are attached to the agitator shaft S, and move over the surface of the plate, alternately covering and uncovering the slits, when the handle E is turned. To the lower end of the same shaft is fastened the agitator O, which is turned simultaneously with the arms just mentioned. After the apparatus has been charged, it is evident that by turning the handle the sulphide of iron may be sifted down at pleasure into the acid water below; and the handles and arms are so disposed that when the bungs are uncovered by the handles the slits are covered by the arms. From the generator, the gas passes through the washer R, whose relations to the apparatus, as well as that of the pressure gauge, are evident from the figure. The generator is lined with lead, and the rest of the apparatus, including the bell-metal plate M, with pure tin. The lead lining of the generator is seamless and very heavy, and all the cocks are lined with block tin tubing. Of the various valves, bungs, and stuffing boxes indicated in the figure, it is unnecessary to speak in detail. It is sufficient to say that they are of excellent workmanship, and during a year's trial have kept perfectly tight. The charging bung, B, however, is closed by a safety cap of peculiar construction, which deserves special mention, because it insures the safety of the apparatus. The cap is represented by Fig. 3, and a section is given in Fig. 4. It will be seen by the last that the escape of the compressed gas from the generator through the apertures *d* is only prevented by a thin disk *a*, which is shown in detail by Fig. 5.

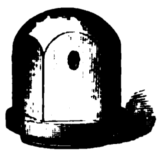


Fig. 3.



Fig. 4.

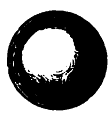


Fig. 5.

This disk is made of two thin plates: the lower one, which comes in contact with the acid spray, is of lead, and the upper one of silvered copper, whose thickness is so adjusted that it must be at once ruptured if the pressure in the apparatus should become unduly great.

Although the so-called soda-water fountains — in which the solution of the gas and water is made — have all in general the same simple relation of parts, they are constructed of very different materials and after very different methods. The outside shell may be either of hammered copper or of some form of iron, and this may be lined with tin, enamel, or glass. After having determined by experiment that a solution of hydric sulphide — especially when some carbonic dioxide is added — exerts no action on a surface of metallic tin, except a very slight and superficial staining, we selected as best adapted to our purpose the steel fountains, also manufactured by the firm of John Matthews, Fig. 6. These are made of plates of steel, united in a

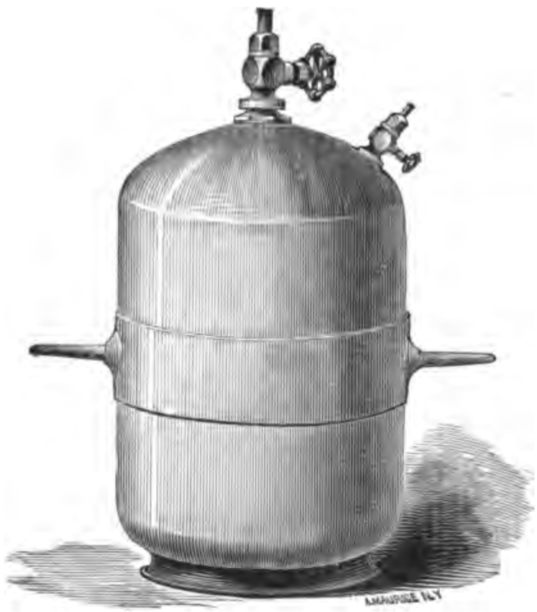


Fig. 6.

peculiar way invented by themselves so as to secure with comparative lightness very great strength. They are lined on the inside with sheet tin, and the tin lining forms an independent vessel, which alone is connected with the bungs. The tubes and valve cocks are also either made or lined with tin, so that the solution never comes in contact with any other metal. For making ordinary soda-water, the fountain requires only a single valve, which connects with a tube leading to the bottom of the vessel, and this serves both to charge the fountain and to draw

off the solution when made. But since a solution of hydric sulphide is rendered turbid if left in contact with even a small quantity of air, and since a variable amount of free hydrogen is always formed by the action of sulphuric acid on common sulphide of iron, it was necessary for our purpose to add to the ordinary fountain a vent cock as shown in the last figure. This enables us to connect together several fountains after the manner of Woolf's bottles as already described, and, by passing the current of gas through the whole line, to drive out all the air originally in the apparatus, as well as the free hydrogen subsequently evolved. Moreover, in the preparation of the solution of hydric sulphide, the generator should be much larger relatively to the fountains than in the preparation of soda-water. Thus we use for charging the so-called six-gallon steel fountains, the "Upright Generator" known as No. 40, which has a capacity below the diaphragm of sixty litres. It should be here stated that the fountains are only rated at two thirds of their total capacity, which is the volume of soda water which is ordinarily made in them. They should never be more than three-fourths filled with water. But, even with this liberal allowance for gas room, the six-gallon fountains referred to will hold twenty-five litres of water. It may also be stated, although the fact must be evident, that a single large fountain will not give as good results as several small ones of equal capacity; since in expelling the air and free hydrogen, as we have described, there would be a considerable loss of material, if only one fountain were used. Still, in laboratories where the consumption is not great, the loss is not important; and the smallest "Upright Generator," with one six-gallon fountain, will be found to be a perfectly satisfactory apparatus.

Assuming first that the larger apparatus is used, the method of charging is as follows: The large generator is too heavy to be readily moved, and should be placed so that the discharge valve will empty directly into a drain. Water also should be brought to the apparatus by hose, — if possible, both hot and cold water, — not only for convenience in charging, but also in washing. Finally, there ought to be a good flue in the neighborhood, into which the waste gas may be discharged. The apparatus having been thus established, the three fountains — first rinsed out — are filled each with twenty-five litres of distilled water, and, the valves having been secured, the fountains are connected with each other and the generator by means of stout rubber hose as already indicated, and the vent valve of the last fountain is connected with the flue by a length of common gas hose. The generator is then charged as follows: The handle is first placed so as to uncover the bungs and cover the slits in the diaphragm. Through the bung A is

now poured 40 litres of *hot* water, heated to between 70° and 80° C., and then 5 litres of common oil of vitriol are poured very cautiously into the same bung through a lead funnel with narrow spout provided for the purpose. The acid water will thus be heated nearly to the boiling point, and its capacity of dissolving ferrous sulphate raised to the maximum. Next 6 kilogrammes of sulphide of iron — previously sufficiently pulverized to pass through a wire sieve with eight meshes to the inch, and mixed with two kilogrammes of marble powder — is run through a wide-mouth funnel into the bung B. The bungs having been now all closed, the joints of the apparatus tested, the exit valve D of the generator and all the valves of the fountains opened, a small amount of the powder is sifted down into the acid water by turning the handle not more than a single revolution, always taking care to leave it so that the slits of the diaphragm shall be left covered. The gas is then allowed to stream through the apparatus, and tested as it escapes into the flue, until it burns without explosion, using a small pneumatic trough for that purpose. The air is now nearly expelled, and the escape of gas should be reduced by the last vent valve until the current only supplies a small jet, which may now be attached and lighted with safety, and by the size of this flame the vent may afterwards be regulated. The handles are now slowly turned, and the pressure in the apparatus carried up to about 120 pounds. The valves of the fountains and the valve D of the generator are now all closed, and the two last fountains detached, leaving the first (which is mounted on a frame as represented in Fig. 1) united to the generator as before. This is now rocked for several minutes to and fro, in order to thoroughly agitate the water with the gas. The stop valve G should then be opened, and then the valve D (very gradually), so that the gas may be admitted slowly to the fountain. The valves are then again closed, and the agitation renewed, and the same operation is repeated several times until no more gas is absorbed by the water in the fountain, the pressure in the generator meanwhile being maintained at 120 lbs., by turning the handle. The first fountain is then removed, and the same process repeated with each of the others. At the close of the operation, after all chemical action has ceased, there remains in the generator — both free and dissolved in the liquid residue — a large volume of hydric sulphide gas. This we economize by venting the generator slowly through Woolf's bottles containing aqua ammonia, and thus preparing at the same time ammonic sulphide. It is not unimportant to add that the generator should be emptied before it cools, and the ferrous sulphate has time to crystallize. The discharge valve R should then be removed, and the whole apparatus thoroughly

washed out. If the valve becomes clogged, it can generally be cleared by developing pressure in the generator by means of a small charge of ground marble. Otherwise, after the pressure has been relieved, and the upper valves and bungs closed, the discharge valve must be cautiously removed, and an opening forced through the lower bung. Such details are necessary in order that others may profit by our experience; but, lest the details should convey the impression that the apparatus is complicated, and that the process requires skilled labor, it may be stated that in this laboratory the apparatus is entirely in charge of a laboratory servant, and may be managed by any workman of ordinary intelligence. It does not require more than four hours to work over a single charge, and this yields 75 litres of hydric sulphide solution under a pressure of 120 lbs. According to our experience, this supply lasts with a class of one hundred students in qualitative analysis about a month. For laboratories where the classes are much smaller than this, we should recommend the smallest size generator, which may be used with a single six-gallon fountain. The smaller apparatus is managed in precisely the same way as the larger, only taking one half the quantity of materials. It is important as before to wash out in the first place all the air, and to maintain a small current of gas through the vent valve of the fountain while the pressure in the apparatus is rising. This of course entails some loss of hydric sulphide; but the chief loss is caused by the venting of the generator, and all this gas may be utilized for the preparation of alkaline sulphides as described above, or this waste gas may be used for washing out the air from a second fountain, and thus preparing it for a subsequent charge.

For dispensing the reagent in our *qualitative* laboratory, we place the fountain in a cupboard and connect it by a block-tin tube with a so called "draught column," Fig. 7, in the ventilating hood above. From this each student draws the reagent as it is required. In quantitative work we may draw the charged water directly from the fountain into the midst of the solution to be treated, using simply a common rubber hose terminated by a glass tube which dips under the surface of the liquid: the hose is attached to the nipple of a cap which screws on to the valve of the fountain, and by confining two or more disks of linen cloth between the cap and the head of the valve (like washers) we can filter the solution as it flows out. It is more convenient, however, to distribute the reagent to advanced students in the well-known soda-water siphon, Fig. 8. These require no description, but as the simple apparatus used for filling the siphon is not yet a familiar object in chemical laboratories, we give a figure of the

apparatus (Fig. 9), taken, like our other cuts, from the catalogue of John Matthews. By pressing the foot on a pedal shown at the base

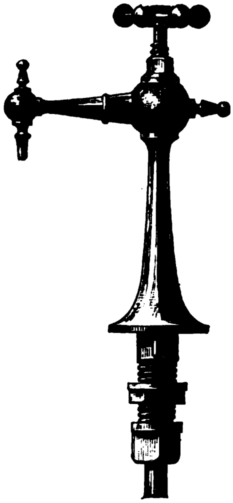


Fig. 7.



Fig. 8.

of the apparatus, the siphon — confined in a cage — is raised, so that its mouth is forced tightly against one opening of a valve of peculiar construction, the second opening of which is united by a block-tin tube to a fountain; while at the same time the handle of the siphon is pressed back. On now pushing the upper lever shown in the cut to the right, the valve of the fountain having been previously opened, a connection is made between the fountain and the siphon; when the charged water rushes into the latter, condensing the air to a fraction of its original volume. If next the same lever is pushed momentarily to the left, the first connection is closed; while a vent is opened, through which the condensed air rushes out into the atmosphere before the gas in solution has time to escape, and then on pushing back the handle a further portion of liquid enters, nearly filling the interior of the bottle. Lastly, on raising the foot, the valve of the siphon shuts at the same time that the bottle is lowered and released from its cage, — the whole process being the work of a few seconds. At the first filling, there sometimes remains a small amount of air in the siphon, so that the solution becomes slightly turbid on standing; but this effect of oxidation can be easily avoided by using a sufficient amount of marble powder

in charging the generator. This siphon unquestionably affords the most convenient mode of using hydric sulphide; and for a private laboratory a single siphon, well charged, will afford as ample a supply as will ordinarily be needed. It is greatly to be hoped that our manufacturing chemists may soon find an advantage in supplying this important reagent in such an elegant form.*



Fig. 9.

When the water is charged as directed above, it of course holds in solution, besides hydric sulphide, a considerable volume of carbonic dioxide; and if, under any circumstance, the presence of this last gas would produce an injurious effect, the marble powder can be simply omitted in charging the generator. In almost all cases, however, the carbonic dioxide exerts a very beneficial influence, and in several ways. In the first place, it insures the non-action of the hydric sulphide on the metallic surfaces of the apparatus. In the second place, it protects the solution from the action of the air when it is drawn into an open vessel, so that after a metallic sulphide has been precipitated by an excess of the reagent, the products may be digested in an open flask or beaker without fear of oxidation. In the third place, the carbonic dioxide adds greatly to the tension of the confined gas, and enables us to develop sufficient pressure to charge the siphon without unnecessarily increasing the strength of the solution of hydric sulphide.

Chemical Laboratory of Harvard College, 1876.

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* All the apparatus here described may be obtained from the firm of John Matthews, First Avenue, 26th and 27th Streets, New York, at very reasonable rates. Be careful in ordering to state the use to which the apparatus is to be put, with the caution that no silver plating or lead paint should be used upon it.

IX.

ON THE PROCESS OF REVERSE FILTERING AND ITS APPLICATION TO LARGE MASSES OF MATERIAL.

BY JOSIAH P. COOKE, JR.,

Erving Professor of Chemistry and Mineralogy in Harvard College.

Presented May 30, 1876.

BY reverse filtering is meant a process of filtration in which the liquid to be filtered is drawn upwards instead of flowing downwards in the usual way. Such a system is often used in the arts, as when a porous septum is attached to the mouth of a suction pipe; or as in the small portable filters so useful to travellers, by which clear water may be sucked up from a muddy pool or turbid stream. These last suggested the application of the same principle in chemical analysis to the treatment of those precipitates which are usually weighed on a dried filter. In such cases, it is of course essential that the weight of the paper disk used as a filter should remain invariable; and this constancy can be best secured by making the disk as small as possible. If the filter is large, it is impossible to have any confident assurance of the constancy of its weight, however great the care that may be taken to secure a similarity of hygrometric conditions at the two weighings; and hence it has not hitherto been practicable to determine on a dried filter the weight of any considerable quantity of a precipitate with accuracy. But, in the process of reverse filtering, we can both wash and collect very large masses of precipitates with a filter not more than an inch in diameter; and if, before drying, these little disks of paper are soaked in dilute hydrochloric acid, and afterwards thoroughly washed in water, their weight remains practically invariable. Indeed, it is not necessary to enclose the filter in a weighing tube, or to pay any special regard to its hygrometric conditions other than to keep the usual drying materials in the balance case. The only liability to alteration of weight would arise from the dissolving of soluble material in the paper, and this may be wholly prevented by previously washing the disks as just described.

In the early part of 1873, having occasion to determine large quan-

tities of sulphide of antimony, we in the first place employed the porous filtering cones described by Prof. C. E. Munroe; * but we found these both too limited in capacity, and too susceptible to hygroscopic influences, to give the degree of accuracy we required. We were therefore led to devise the following apparatus, which Figures 1 and 2 will help us to describe. The most essential part of this apparatus is the platinum "rose" represented by Fig. 1. This is cemented by sealing-wax to the end of a glass tube, and to its perforated base the small filters are applied. The glass tube is so cemented into the neck of the "rose" that the end may reach quite down to the perforated plate, and thus draw up all the liquid which collects in the hemispherical cup. Moreover, the perforated plate has an unbroken rim about $\frac{1}{16}$ of an inch wide around the edge, which is sufficient to prevent any solid particles from creeping by the edges of the paper disk. The success aud rapidity of the filtering depend on the proper construction of the perforated disk, and we obtained the best results only after several trials. The holes should be smoothly perforated about $\frac{1}{50}$ of an inch in diameter, and as numerous as possible, leaving the unbroken rim described above. After the perforations are made, the face of the plate should be ground perfectly smooth. We use two sizes of these "roses," in one of which the hemisphere is $\frac{15}{16}$ of an inch, and of the other $1\frac{1}{4}$ inches in diameter; but the smaller is the more useful, and is sufficiently large for all ordinary purposes. A disk of washed Swedish filtering paper, $\frac{15}{16}$ of an inch in diameter, weighs only about 20 milligrammes; and, to give an idea of the rapidity of the filtration, it is sufficient to say that, under a pressure of 50 centimetres of mercury, these filters will pass from 20 to 30 litres of clear water in an hour. We have been greatly indebted to Messrs. Johnson, Matthey, & Co., of Hatton Garden, London, for the care they have taken in the construction of these "roses;" and they can be procured of them through the mail. The cost of the smaller size is fifteen shillings sterling. The construction of the rest of the apparatus is made clear by Fig. 2. One of the stems of a glass three-way tube is clamped to an arm which can be raised or lowered on the vertical bar of an elevating stand by a rack and pinion movement, which ought, however, to be so loose, that the arm can be pushed suddenly up when necessary. By its second stem, the three-way tube is connected

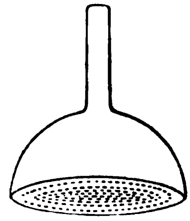


Fig. 1.

* American Journal of Science, May, 1871.

by a rubber hose with a large glass bottle, in which a partial vacuum is maintained by a Bunsen pump, but this connection can be closed by



Fig. 2.

a compression cock. The third stem, which makes a connection with the atmosphere, is closed by a rubber connector and nipper tap, and serves to suddenly relieve the pressure in case the filter slips or breaks. From the first and vertical stem of the three-way tube below the clamp is suspended the glass tube, having the rose at its end. The suspension consists of a rubber connector, so long that it can be bent double and the rose inverted, and so stout that when thus bent the connection with the bottle is completely closed. When inverted, the tube of the rose rests against the thumbscrew of the pinion, and is thus confined.

In order that we may make clear the mode of using the apparatus, let us assume that five grammes of antimonious sulphide have been precipitated in a glass beaker, holding two litres of liquid, and that the precipitate has settled, — as it will after boiling, — leaving the supernatant liquid perfectly clear. A partial vacuum having been formed

in the bottle, and the beaker having been placed on the stand, we begin by attaching the paper disk to the base of the rose, moistening it for the purpose with water, and forcing it with the thumb against the perforated plate until the adhesion is complete at every point. It is important that the disk should not overlap the edge of the plate; and, if the plate has been made as described, it will adhere tightly without so doing. The compression cock is then slowly opened; and, as soon as the sound indicates that the air is being sucked through the filter, the base of the rose is quickly sunk under the liquid, and constantly lowered by the rack and pinion movement, as fast as the liquid is drawn off. The supernatant liquid may thus be decanted until the rose is close down to the precipitate; but care should be taken at this stage not to push the process too far, lest the filter should become clogged by the adhesion of solid particles, as would be the case, if it comes too near the level of the precipitate. When the safe level has been reached, the arm of the stand is suddenly pushed upwards, while the rose is inverted and supported as above described. The beaker is now filled up with hot water; and, after the precipitate has subsided, the wash water is drawn off as before, and so repeatedly as often as may be necessary. It is important, however, to carefully watch the filter, and every time before immersing the rose to see that the paper is moist and firmly adhering to the perforated plate. It is further essential that the suction should not be for a moment interrupted while the filter is immersed. This condition is secured by the simple rubber joint we have described; for, while when the rose is inverted the connection with the bottle is closed, the moment it is turned down the connection is opened, and the filter begins to draw. If, however, by any accident the filter should slip, the operator when on his guard can avoid loss of material by quickly opening the nipper tap, and relieving the pressure until the rose can be withdrawn and washed out. The filter can then be fished out with a glass rod, washed off and replaced. A good strong filter will bear quite rough treatment; and, if in the process it becomes clogged, it can be taken off when the rose is inverted, and the adhering precipitate washed back into the beaker. When replaced, the paper thus cleansed often filters as rapidly as before. If, as is sometimes the case, the paper becomes hopelessly clogged, no great loss of accuracy is suffered by using a second or even a third filter. Of course, they must all be dried, and weighed either with the precipitate or apart, as most convenient.

The precipitate, having been thus washed, is next to be transferred to the crucible in which it is to be weighed; and, to hold five grammes

of precipitated antimonious sulphide, we shall require a crucible having a capacity of 250 cubic centimetres. As much of the water as can readily be decanted from the precipitate is first poured into the crucible and drawn off with the filter, and then the precipitate is washed in with as little additional water as possible. Now the filter is plunged into the semi-fluid mass, and must not afterwards be removed until the process is completed. The rose ought not even to be raised however slightly, although additional material may be poured in around it. As the mass contracts in the crucible, the filter must be made to follow, always keeping it immersed; and during this time the precipitate which has collected around the platinum rose may be washed down by a stream from a wash bottle. In this way the greater part of the water can be removed, leaving the precipitate nearly as compact as it is left on a common filter, when dried by Bunsen's pump. When the precipitate is in this condition, the pressure is relieved by opening the nipper tap, and the rose raised, which leaves the filter behind. If any of the precipitate has clung to the platinum, this must now be washed into the crucible with a few drops of water, the rose and tube having first been detached from the connector for the purpose. It only now remains to dry the precipitate with the little filter, and weigh it. If it is important to dry the precipitate at a temperature above 150° C., or even to ignite it, the mass should first be thoroughly dried at 100°. The little disk of paper can then be removed and weighed separately, while the rest of the mass is heated to a higher temperature. The amount of material which remains adhering to the paper under these circumstances is exceedingly small, not usually exceeding a few milligrammes; and allowance can be made for it in the final result, without sensible error.

Like other analytical processes, this method has its limits; and any attempt to extend it beyond the sphere of its usefulness will lead to unsatisfactory results. It is of no use for filtering turbid liquids, since the small filters are rapidly clogged, and the process becomes proportionally slow. Whenever, however, a precipitate settles clearly, this method enables us to wash, collect, and weigh very large quantities of precipitates in a very short time with wonderful accuracy. We have used it chiefly to determine sulphide of antimony and chloride bromide or iodide of silver; and the results of the following analyses, extracted from our forthcoming paper on the Atomic Weights of Antimony, will show how great accuracy can be attained with it: —

SYNTHESIS OF SULPHIDE OF ANTIMONY.

Weight in Grammes of Sb taken.	Weight of $Sb_2 S_3$ dried at 180° C.	Per cent of S in same.
2.1439	3.0025	28.58
2.3417	3.2792	28.59
2.2182	3.1061	28.59

ANALYSIS OF ANTIMONIOUS CHLORIDE.

Weight in Grammes of $Sb\,Cl_3$ taken.	Weight of AgCl obtained.	Per cent of Chlorine
2.0300	3.8282	46.652
1.3686	2.5813	46.659
1.8638	3.5146	46.651

ANALYSIS OF ANTIMONIOUS BROMIDE.

Weight in Grammes of $Sb\,Br_3$ taken.	Weight of Ag Br obtained.	Per cent of Bromine.
1.2124	1.8991	66.655
0.9417	1.4749	66.647

These analyses exhibit a fair sample of the results which can easily be obtained with this method. In order to assure ourselves that the weight of the small paper disks remained constant, we have repeatedly dissolved off the small amount of adhering precipitate, and after washing and drying reweighed the disks at the completion of the analysis. Even with the larger disks there was in no case any material change in the weight, and in most cases no alteration whatever could be detected with a balance turning readily with $\frac{1}{10}$ of a milligramme.

The method of collecting precipitates here described, which, as we have shown, is so useful where considerable quantities are to be estimated, is equally applicable to very small amounts. When the quantity of the precipitate does not exceed a few milligrammes, the whole becomes fastened by the suction to the surface of the paper. There is then, of course, no need of a crucible in the process. The filter, having been dried in a watch glass, is weighed by itself, and a result of very great accuracy is reached with great rapidity. We have in this way frequently estimated minute quantities of baric sulphate and argentic chloride, whose weight proved to be only a fraction of a milligramme.

Although the apparatus here described and figured was invented independently by myself in order to overcome difficulties, already stated, which I met with in the course of my investigations, yet in its main features I was anticipated by Professor H. Carmichael, now of Bowdoin College; and I had the misfortune not to have my attention called to his paper on the subject — dated at Göttingen, 1870, and published in the Zeitschrift für Chemie, neue Folge, Band VI., 481 — until long after my own apparatus had been perfected. But although Professor Carmichael and myself started from the same fundamental idea, yet we have worked this idea out in very different forms, and with very different purposes in view. While therefore I would acknowledge most fully Professor Carmichael's priority, I have thought it best to publish this paper with the sole object of adding to his previous work the results of my own experience, and with the hope that I may thus aid in introducing into analytical laboratories what I believe to be the most important improvement in analytical chemistry which has been made since the invention of the Bunsen pump.

CHEMICAL LABORATORY OF HARVARD COLLEGE, 1876.

PROCEEDINGS

OF THE

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OF

ARTS AND SCIENCES.

VOL. XIII.

PAPERS READ BEFORE THE ACADEMY.

I.

REVISION OF THE ATOMIC WEIGHTS OF ANTIMONY.

BY JOSIAH P. COOKE, JR.,
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THE first determination of what we now call the atomic weight of antimony was made by Berzelius, and the result published in 1818.* His method consisted in oxidizing the metal with nitric acid and igniting the residue. This product he called antimonious acid; and, after a careful study of the chemical relations of the several oxides and of the native sulphide of antimony, he assigned to antimonious acid the symbol $Sb\,O_4$, that of the basic oxide being $Sb\,O_3$, and of the native sulphide $Sb\,S_3$. In some earlier experiments,† Berzelius had not obtained constant results with the same process, 100 parts of "pure antimony" having yielded in four experiments 125.8, 126, 127.5, and 127.8 parts of antimonious acid respectively; but in his later paper he attributes the discordance to the circumstance that he had previously conducted the process in glass flasks, "which could not bear a sufficiently strong heat to change all the yellow residue into white oxide." By the later experiments, in which platinum vessels were used, he found that 100 parts of antimony yield 124.8 parts of antimonious acid. But although he distinctly states "that when pure antimony is oxidized

* Schweigger Jour. für Chem. und Phys., xxii. 70, 1818.
† Ibid., vi. 149, 1812.

in a flask with nitric acid, and the mass evaporated to dryness in a platinum crucible is heated until it becomes perfectly white, the same results are always obtained," nevertheless, in the paper cited, he does not give the several determinations on which his conclusion was based, or any details by which we can now judge of the purity of the metal used. He simply gives the single result just cited, from which we readily deduce as the atomic weight of antimony 129; and with this value he appears to have been contented; for we find in his masterly review of the atomic weights of the chemical elements, published in 1826,* the same value given, without further comment, and it remained unquestioned for more than thirty-eight years.

Not until 1856 does any further investigation of the subject appear to have been made. In February of that year, R. Schneider, of Berlin, published a preliminary notice; † and later, in May, the full details‡ of a new determination of the atomic weight of antimony, made by a method wholly different from that of Berzelius. This method consisted in reducing a pure native sulphide of antimony by hydrogen gas. The material selected was the antimony glance of Arnberg, which is distinguished for its high degree of purity, and by appropriate tests the mineral was shown to be free from arsenic and the metals which usually accompany antimony. The only impurity that could be discovered was a small amount of quartz, which is associated with the mineral as gangue; but this was of no importance, since the amount could be determined in every experiment with almost absolute precision. The same was almost equally true of two well-known defects in the process, which, if not allowed for, would become sources of error; namely, the escape in vapor, or, mechanically, of a small amount of sulphide of antimony during the reduction, and the circumstance that a further small amount of sulphide escapes reduction by becoming enclosed in the regulus. The first of these effects would diminish, and the second increase, the weight of the regulus; and the same effects would also respectively diminish or increase the atomic weight of antimony calculated from the observations. The two sources of error evidently tend to balance each other; but, on the other hand, the effect of the last is several times greater than that of the first. The total effect, however, is but small; and, had these known sources of error been

* Poggendorff's Annalen, viii. 23, 1826.
† Ibid., xcvii. 483, February, 1856.
‡ Ibid., xcviii., 293, May, 1856.

wholly overlooked by Schneider, the effect would only have been to raise the mean result about 0.26. So far, however, from neglecting these very small errors, Schneider in every case accurately collected and determined both the sulphide of antimony volatilized and the sulphur retained by the regulus, and with these amounts, never exceeding a few milligrammes, he corrected his observed data. In the paper referred to, Schneider gives the detail of eight separate determinations, the mean of which gives for the atomic weight of antimony the value 120.30, and this differs from the extremes on either side by only 0.23. In this determination, the atomic weight of antimony is referred to that of sulphur, which is taken as 32.*

In the next number of Poggendorff's "Annalen" to that in which the paper of Schneider appeared, Heinrich Rose published the result of a previous analysis of $Sb\,Cl_3$, made under his direction by Herr Weber, which gives for the atomic weight of antimony the value 120.7 when chlorine is 35.5; and, although we have only the evidence of a single analysis, yet this one was thought by Rose to be of especial value as confirming the subsequent determination of Schneider. This confirmation he regarded as the more satisfactory, since by Weber's analysis the atomic weight of antimony is referred to chlorine, and not as before to sulphur or oxygen. The process was this: A weighed amount of $Sb\,Cl_3$, purified by repeated fractional distillation, was dissolved in an aqueous solution of tartaric acid. From this solution the metal was precipitated by H_2S, and in the filtrate the chlorine was determined by precipitation with $AgNO_3$ in the usual way.

Next in order in this series of investigations comes the admirable work of Mr. W. P. Dexter. He adopted the same process as Berzelius, but conducted it with all the refinement which ingenuity, guided by the increased chemical knowledge of the time, could devise. Especial care was taken to secure pure metallic antimony; and a comparison of the results obtained with different specimens — purified by the processes he describes — shows conclusively that, even if the metal was not absolutely pure, the error resulting from this cause was wholly inappreciable. The agreement between the results of the several experiments is wonderfully close, but for the details we must refer to the original paper.† It is only important to state here that Dexter obtained for the atomic weight of antimony, as the mean of ten determinations, the value 122.34, and that the extremes on either side were

* Poggendorff's Annalen, xcviii. 455, June, 1856.

† Ibid., c. 563, April, 1857.

122.24 and 122.48. The difference between these extremes corresponds to only 1 milligramme in 3 grammes of Sb_2O_4, which was about the average amount weighed in these experiments.

In June, 1861, F. Kessler, of Dantzic, published in Poggendorff's "Annalen" a paper * devoted to a re-examination of the atomic weights of chromium, arsenic, and antimony, based on a method of volumetric analysis which he had previously described in the same journal.† Indeed, in his earlier paper he had already quite fully elaborated the subject, and thus anticipated both Schneider and Dexter in correcting the old number of Berzelius. The method of Kessler was based on the reciprocal relations of potassic dichromate and ferrous chloride; and, as is well known, standard solutions of these salts are especially well adapted to volumetric determinations, by the circumstance that the neutral point can be so accurately fixed by the reaction with potassic ferricyanide. For the details of the method, which were quite numerous and complicated, we must refer to the original paper. It is sufficient for the present purpose to say that the atomic weight of antimony was thus indirectly referred to the molecular weight of potassic chlorate, which was taken as 122.57, according to the determinations of Pelouze and of Marignac. Kessler experimented with antimony, with antimonious oxide, and antimonious chloride, and obtained results varying between 121.67 and 122.61. We translate his own commentary: "Although the results of these experiments, taken as a whole, agree very nearly with those obtained by Dexter, I must nevertheless confess that I am not wholly convinced that our number, which is two hydrogen units higher than that found by Schneider, is much nearer the truth than his. Every one who has occupied himself with the analysis of different antimony compounds must be able to indorse what Berzelius wrote in 1812: 'I have never worked with a material with which it was so extremely difficult to obtain constant results.' . . . Nevertheless, I believe I have been able to show that in the analysis of antimony compounds the volumetric method is capable of affording a very sharp control over results obtained in other ways."

Before the Académie des Sciences in Paris, in 1857 and 1858,‡ Dumas read the results of his celebrated revision of the atomic weights of the chemical elements, during which he redetermined the atomic weight of antimony.§ With this, as with most of the other elements

* Poggendorff's Annalen, cxiii. 134, June, 1861.

† Ibid., xcv. 204, June, 1855.

‡ The 9th of November, 1857, and the 27th of December, 1858.

§ Annales de Chimie et de Physique, 3me Séries, LV. 175, February, 1859.

whose atomic weights he redetermined, his process consisted in analyzing the chloride ($SbCl_3$) and weighing the chlorine as argentic chloride. The antimonious chloride was prepared by the action of dry chlorine on pure antimony, — "de l'antimoine très-pur et du chlor sec," — and purified by repeated distillations over the metal in fine powder. A weighed amount of this chloride was added to a solution of tartaric acid in water, and the chlorine directly precipitated in the usual way. Dumas adds: "Je n'ai entrevu ni apparence de cause d'erreur particulière, ni irrégularité dans les résultats." He gives four determinations as follows: —

1.	1.876 of $SbCl_3$	correspond to	2.660 Ag;	hence Sb	= 122.00
2.	4.336	„	„	6.148 „	„	= 122.00
3.	5.065	„	„	7.175 „	„	= 122.20
4.	3.475	„	„	4.930 „	„	= 121.94

The first three were from the same, but the last from a different preparation. From these results, Dumas deduces as the most probable value of the atomic weight of antimony the whole number 122, and this differs from the extreme value obtained by only 0.2. It will be noticed that the method of Dumas is essentially the same as that of Rose, only the former did not separate the antimony from the solution before precipitating with argentic nitrate. This, however, may be an important difference; for, as we shall show hereafter, an excess of argentic nitrate, added to a solution containing antimonious chloride and tartaric acid, above the amount necessary to precipitate the chlorine, determines the formation of argento-antimonious tartrate, which slowly crystallizes out from the solution on standing, and is almost wholly insoluble in cold water. The occlusion of this material by the precipitated argentic chloride on the one hand, and on the other hand the slight solubility which we also noticed of this precipitate in the resulting menstruum, gave us a very different impression of the accuracy of the process from that obtained by Dumas. Rose, however, does not mention these possible sources of error. It seems probable that Weber, under his direction, aimed to estimate the antimony as well as the chlorine of the compound analyzed, and for this reason precipitated the antimony first. Moreover, the chief of the causes of error we have noticed would tend to lower the observed atomic weight of antimony; and our experience would lead us to question whether the previous precipitation of the antimony would not occasion more error than it prevents.

The only other determination of the atomic weight of antimony

which has come to our knowledge was made incidentally by B. Unger* while studying the chemical relations of Schlippe's salt, $Na_3S_4Sb \cdot 9\, H_2O$. An analysis of this salt gave Sb = 119.76, when S = 32 and Na = 23 ; but this value rests on a single experimental determination, by a method from which great accuracy could not be expected.

As is well known, the value 122 obtained by Dumas is the one which is almost universally accepted as the atomic weight of antimony, and this not only in consequence of the deservedly great authority of this distinguished experimenter, but also because his result so nearly agrees with the previous determination of Dexter. Nevertheless, a careful examination of the work of Schneider, referred to above, will convince every chemist that it is impossible to refer the difference between 120.3, the number he obtained, and 122, to any experimental errors. This difference is nearly one and a half per cent of the whole value; although it is evident that the probable experimental error does not, in either case, amount to one tenth of one per cent. Moreover, it will be found that this investigation of Schneider is a model of its kind. All the details of the experimental work are given, and it is evident that every precaution was taken which the circumstances required. Furthermore, the method of Schneider has a very great advantage over all the processes by which the atomic weight of antimony has been determined, in that he was able to obtain satisfactory evidence, not only of the purity, but also of the definite atomic composition of the material he analyzed. In the determination of an atomic weight, it is not only essential that the substance selected for analysis should be pure, in the sense of containing no adventitious elements : it is even more important that neither of the constituents whose atomic ratio is to be determined should be present in excess of the normal proportion. But, while experimenters have been most careful to establish the purity of their material in the first sense, they have seldom given a thought to the possibility of such an impurity as the preponderance of one or the other of the proper constituents of the compound practically constitutes. Theoretical considerations, based on the law of definite proportions, might lead a chemist to believe that impurity in the last sense was impossible in a true chemical compound. But how are we to know that a given material is of the true type? It is certain that the ordinary physical tests of purity, such as the melting point and the boiling point, are insufficient; and the same is equally true of the perfection of crystalline form, that character on which of all others the

* Archiv. der Pharmacie, 1871, Band 197, S. 194.

chemist most frequently relies. As early as 1860, we ourselves showed that constancy of crystalline form was, under certain conditions, compatible with quite wide variations of compositions; * and our conclusions have been most fully confirmed by the results of investigations since made, which reveal the great complexity of crystalline structures. In the compounds † of zinc and antimony which we investigated, the variation was large, because the affinity was weak; but we gave abundant evidence that similar variations, although of less extent, are not uncommon in more stable compounds, and from our subsequent experience we feel confident that in proportion as analytical processes become more accurate these variations will become more apparent. At present, they are to a great extent concealed, because the possible errors of our analytical processes are so great; and we very properly refer, at the outset, any seeming variations from exact atomic proportions to errors of this class. But, in the more accurate methods on which we should alone rely for fixing atomic weights, such variations, when they exist, become of great importance. For call by whatever name you please that small portion of either constituent of a compound which may be present in a crystal over and above the atomic ratio, — regard it merely as so much "dirt" entangled by the crystalline structure, —

* Crystalline Form not Necessarily an Indication of Definite Chemical Composition. Philosophical Magazine, June, 1860; also Poggendorff's Annalen, Band cxii. 90; also Memoirs of American Academy of Arts and Sciences, New Series, vol. v. p. 387.

† Rammelsberg has expressed the opinion — Pogg. Ann., cxx. 61, 1863 — that all crystalline alloys are isomorphous mixtures of the constituent metals, and includes under this category the two compounds of zinc and antimony here referred to; but, had this accurate observer repeated our experiments and measurements, he would have seen that the whole order of the phenomena we studied is inconsistent with such an assumption. Although the two metals may be alloyed in all proportions, yet we give in our paper the strongest evidence that the union is attended with definite chemical action, which has two maxima at the points represented by the symbols Sb_2Zn_2 and Sb_2Zn_3; and although the measurements of the two sets of crystals may be referred approximately to the same fundamental form, as is frequently the case in the simpler systems, especially if we admit such ratios as 4:5, yet the two types of crystals differ completely in their habit, and the very remarkable circumstances of their formation prove that they are essentially distinct. For a full statement of these circumstances we must refer to our original paper above cited. In the very partial abstract from this paper — Pogg. Ann., xcvi. 584 — to which Rammelsberg alone refers, none of these important facts were given; and, moreover, Rammelsberg does not seem to have noticed that our paper published in 1855 preceded Schneider's determination of the atomic weight of antimony.

yet so long as it is there, and your analytical processes do not distinguish it from that portion of the same element which is chemically combined, it is obvious that impurity of this kind will vitiate your result to a far greater extent than an equal amount of wholly foreign admixture; and of what use can it be to refine processes or multiply and discuss observations, if so large a door is left open to constant errors? Moreover, it must not be overlooked that such errors, from their very nature, are apt to have a constant value, and are for that very reason the more liable to deceive. In the investigation just referred to, we showed that under constant conditions the composition of the crystals was definite and invariable, although they might contain — as dirt or impurity, very possibly — an excess of one or the other elementary substance when compared with the normal atomic proportion. Assuming, then, such an excess to be present in the substance selected for analysis, it is perfectly evident that a large error might exist in the determination of an atomic weight, although there was a close agreement in the analytical results. Such agreement therefore is in itself no proof of accuracy; and far less sharp results may be more trustworthy, if only it can be shown that the errors are properly distributed. Errors of the last class can be to a great extent eliminated by multiplying observations, while a constant error is only perpetuated thereby.

The special cause of constant error we have been discussing is one we have specially studied, and one therefore which we naturally select to illustrate the principle we have aimed to enforce. It is not, however, the only cause of constant error which tends to change the apparent ratio between the weights of the various elements of a compound, or the one whose influence is most to be feared in the determination of an atomic weight. Our knowledge of the chemical and physical relations of the materials analyzed, or of the circumstances connected with the processes employed, is in many cases as yet so far from perfect that to a certain extent we work as it were in the dark, and are liable to fall into errors from which only more accurate knowledge could protect our results. As will appear in the sequel, this truth has been forced upon us again and again during the course of the present investigation, and it has led us to bestow upon the work an amount of labor which is far greater than the importance of the results would seem to justify. The experience, however, has left with us a strong conviction on two important points; and we shall describe the several steps in our investigation more in detail than might otherwise seem necessary, in order that the reasons of these convictions may

appear. In the first place, we are persuaded that in the determination of atomic weights it is just such constant errors as we have encountered that are almost solely to be feared, and that the mechanical perfection of our analytical methods is far in advance of our chemical knowledge of the materials and processes we employ. In the second place, we feel assured that no agreement, however close, of results obtained by the repetition of the same process, under the same conditions, gives any certain guarantee of the correctness of the atomic ratio which is sought to be established; and hence that in the present state of science no certain conclusions can be reached in regard to the validity either of Prout's Law or of other numerical relations between the atomic weights of the chemical elements.

We return now to our former position,— that in determining an atomic weight it is of the first importance to show that the compound analyzed is not only pure in the ordinary sense, but also that it contains the elements to be compared in atomic proportions. And, after carefully reviewing the whole subject in the light of our present knowledge, we have been led to the conclusion that the most satisfactory evidence on this point we can obtain is that furnished by a chemical reaction, in regard to which it can be shown that the two elements under comparison are transferred without loss or elimination of material from one combination to another. Now, satisfactory evidence of this kind may be adduced in regard to the method of determining the atomic weight of antimony employed by Schneider. The native sulphide of antimony which he analyzed dissolves in hydrochloric acid with the evolution of hydric sulphide, leaving no residue saving a minute amount of silicious gangue, which can be accurately estimated. If then sulphur is combined in atomic proportions with hydrogen in the gas evolved during this reaction, it must also have been combined in atomic proportions with antimony in the original compound; for otherwise the metathesis could not have taken place without an elimination of the excess of one or the other of the constituents. To this familiar fact, we can add still other evidence which makes the proof complete. In the first place, we have repeatedly verified the statement of other chemists, that when — as is always the case unless great care is taken — an excess of sulphur is precipitated by the action of hydric sulphide on solutions containing antimony, this excess, however small, is eliminated, and remains undissolved when the dried precipitate of Sb_2S_3 is dissolved in pure hydrochloric acid. In the second place, during our investigation of the zinc and antimony compounds above referred to, we prepared artificial crystals of antimony glance containing several per cent of antimony in

excess of the normal proportion. These crystals were made by fusing the native mineral with an excess of metallic antimony, and pouring out the still melted mass from the crucible, after a portion had crystallized. But although the crystals were extremely brilliant, and had at least this outward characteristic of a definite compound, yet, when dissolved in hydrochloric acid out of contact with the air,* the excess of metal was left undissolved in the condition of a fine powder.

For the reasons we have stated, we have always had great confidence in the results of Schneider, while on the other hand we have felt that both in the case of the oxide of antimony weighed by Dexter, and the chloride of antimony used by Dumas, we could not from the nature of the case have any satisfactory evidence that the material analyzed had the exact atomic composition assigned to it. The antimonic oxide is a perfectly amorphous and inert powder, in regard to which we have neither the evidence of physical properties nor of chemical reactions on the point in question. Moreover, our knowledge of the circumstances under which it is formed would lead us to suspect an admixture of a lower oxide in the product, which would be protected from oxidation (during the ignition) by the surrounding mass, and protected to the same degree under the same conditions. Again, in SbO_2 the weight of the oxygen is only about one-fourth of that of the antimony, so that a very small variation in the weight found would make, in the result, all the difference which is in question. In chloride of antimony, on the other hand, the amount of chlorine is nearly equal to that of the antimony; and for this reason, as well as because chlorine can be so accurately determined, this substance would seem at first sight to be the best adapted of all others for determining the atomic weight of antimony. Our experience, however, has not confirmed this first impression; for although we have found no difficulty whatever in obtaining the material beautifully crystallized and free from such impurities as we should ordinarily look for, yet it is so wonderfully hygroscopic and liable to alteration that we have not as yet succeeded in preparing it for analysis under such conditions that we could feel assured that it was wholly free from moisture or the resulting oxichloride of antimony; and although with sufficient labor and ingenuity the difficulties in the way could undoubtedly be overcome, yet a substance which must be guarded with such precautions is not the best adapted for determining an atomic weight. When, therefore, we had devised the

* Antimony is wholly insoluble in hydrochloric acid out of contact with the air.

method of precipitating metallic sulphides, described in the previous volume of this series,* and found that by its means, and also by boiling the liquid, as suggested by Mr. S. P. Sharples,† we could precipitate sulphide of antimony in a condition apparently peculiarly well adapted for accurate determination, we conceived the idea of reversing Schneider's method, and verifying his result by a synthesis of the same material which he analyzed. The event, however, proved that we had undertaken a work of far more difficulty than we anticipated. We have met unforeseen obstacles at almost every step of our investigation, and have had constant occasion to indorse, with Kessler, the opinion of Berzelius quoted above.

In the preparation of pure metallic antimony, we were greatly guided by the experience of Mr. Dexter; ‡ and our several products must have been very similar to his, as the following determinations of the specific gravities of the different buttons show. The observed values were reduced to 4° C., on the assumption that the coefficient of cubic expansion for antimony between 0° and 100° C. is for each degree 0.000033, as observed by Kopp. The letters here given will be used throughout the table to designate the various specimens. As might be supposed, the specimens were prepared at different times and at different stages of the investigation, but the results are united here for the convenience of comparison and of reference.

SPECIFIC GRAVITIES OF BUTTONS OF PURE METALLIC ANTIMONY.

Observations of J. P. C., Jr.		Observations of W. Dexter.	
A	6.7025	b	6.7087
B	6.7036	c	6.7026
C	6.6957	c	6.6987
D	6.7070	d	6.7102
E	6.7022	e	6.7047
F	6.7023	e	6.7052
Mean	6.7022	Mean	6.7050

* On a New Mode of Manipulating Hydric Sulphide, vol. xii. of these Proceedings, p. 113.

† American Journal of Science and Arts, Second Series, vol. l. p. 248.

‡ Poggendorff's Annalen, Band 100, Seite 564 (*loc. cit.*).

Specimen A was prepared from potassic antimoniate (marked Robiquet and Pelletier, *pur*). A solution of the salt in water was filtered into a similar hot solution of sodic carbonate. The precipitated sodic antimoniate was thoroughly washed with hot water, then dried, and reduced with potassic cyanide. Lastly, the regulus was remelted, and kept in fusion for several hours under its own oxide. Specimen B was prepared, in a similar way, from potassic antimoniate (marked Rousseau Frères, *pur*). Specimen C was prepared from commercial antimony. The metal was first oxidized, and the oxide boiled with an excess of pure nitric acid. The oxide was afterwards repeatedly washed with boiling water, and, when dried, was reduced with potassic cyanide. A third of the resulting metal was again oxidized with nitric acid; and this oxide having been first mixed with the rest of the metal, previously pulverized, the mixture was kept melted for a long time in a covered crucible. The purified metal thus obtained was again fused in a porcelain crucible, under its own oxide, for several hours. Specimen D was the residue of C, — part having been used for casting bullets, — again fused for several hours under its own oxide. Specimen E was prepared by the process described above from potassic antimoniate, made by ourselves from commercial antimony. It was fused for four hours under its own oxide. Specimen F was prepared by Liebig's well-known process, and further purified by fusing the regulus for twenty-nine hours under its own oxide. It is unnecessary to add that these fusions were all made in porcelain crucibles, and that only the purest reagents were employed in the various processes, except only in the early stages of the preparation of C and F. These last preparations were both used for casting the antimony bullets with which the solutions of the metal were reduced before precipitating with H_2S, as will be described hereafter.

We give, in a parallel column with our own results, the specific gravities, determined by Mr. Dexter, of the specimens of pure antimony prepared by him, and used in his determinations of the atomic weight of this element. It will be noticed that the agreement is very close, the mean of his results not differing from that of ours as much by one-half as either set differ among themselves. These differences are evidently owing to slight variations in homogeneity, due to the crystalline structure of the metal. This is made probable by the following results which we obtained with specimen F, prepared as described above by Liebig's process. This was repeatedly fused in its own oxide, and the specific gravity taken at each stage of the process.

SPECIFIC GRAVITY OF SPECIMEN F.

After five hours' fusion, additional . . .	6.7050
" " " " " . . .	6.6977
" " " " " . . .	6.6959
" " " " " . . .	6.6840
" nine " " " . . .	6.7022
" several " " " . . .	6.7012

Such irregular variations as these could obviously not be referred to a gradual change in the purity or composition of the metal.

Of the several processes employed for purifying antimony, the last is the easiest, yields the largest product, and is as effectual as either of the other two. The long fusion of the metal under its own oxide can in no case be avoided, as this is the only sure method of removing the last traces of iron, at least so far as our experience extends. In repeating the work, however, we should prefer to start from antimonious chloride, prepared from antimony glance. This can easily be purified by repeated distillation, and is absolutely free from arsenic, which cannot always be said of the metal obtained by Liebig's process.

To bring a *given quantity* of antimony into solution, so that the whole shall be left in its condition of lowest quantivalence, and therefore be precipitated by H_2S as antimonious sulphide, without the least excess of sulphur, we found to be a very difficult task; nor have we succeeded invariably in effecting this result, except by the indirect method hereafter described. Finely powdered antimony dissolves readily when digested with a concentrated solution of tartaric acid, to which a few drops of nitric acid have been added; but from such a solution, even after the remaining nitric acid has been carefully neutralized, free sulphur is always precipitated with the sulphide of antimony; and, although we tried various ways, we were unable to find any process by which this effect could be wholly prevented. Very singularly we obtained the best results by acting on antimony directly with nitric acid, under such regulated conditions that the metal was wholly converted into antimonious nitrate, and subsequently removing the excess of acid by slow evaporation at a temperature below 100° C. If the conversion is successfully accomplished, then, on adding to the crystalline residue a strong solution of tartaric acid, this residue is at once dissolved, giving a perfectly clear solution, in which the metal is almost wholly, if not entirely, in its lower condition of quantivalence. The difficulty consists in regulating the action of the nitric acid. We succeeded best by using acid of the sp. gr. 1.35, which we added in large

excess to the powdered antimony, previously moistened with water, and as soon as, on gently heating the beaker, the action began, we kept the mass in constant agitation, so as to prevent the temperature from rising too high at any point. If during this reaction, or during the subsequent evaporation of the excess of acid, the dry nitrate is heated even to 100°, decomposition ensues, and higher oxides are formed, which are insoluble in tartaric acid. Indeed, this is probably the order of the change even during the violent action of nitric acid on antimony, when antimonic oxide, Sb_2O_4, is the chief product, antimonious nitrate being in all cases formed first, and subsequently decomposed. Unfortunately, we could not always succeed in obtaining a clear solution in this way; and the loss of pure material occasioned by the unsuccessful trials was so considerable that we soon abandoned the method. Still, it was capable of yielding good results, as the determinations given below will show.

The rest of the process was as follows: The tartaric acid solution having been brought to the proper degree of dilution, — about 250 cubic centimetres to each gramme of antimony, — the free acid was first carefully neutralized with pure caustic soda. A small amount of hydrochloric acid was next added, and the antimony precipitated with H_2S. In these, as well as in all the subsequent determinations, the precipitation was conducted thus: The solution having been made in a large Erlenmeyer flask, and this firmly supported over a gas lamp, a current of washed carbonic dioxide gas was conducted into the liquid from a suitable generator, the glass tube conducting the gas reaching to the bottom of the flask, so that the gas might bubble up through the whole column of liquid. The atmospheric air having been thus completely expelled, then, through a second glass tube similarly arranged, an excess of a supersaturated solution of H_2S was drawn into the vessel from the fountain or siphon described in the paper above referred to. The temperature of the mass was now slowly raised to the boiling point, and the liquid actually boiled for ten or fifteen minutes. The current of carbonic dioxide, continually passing meanwhile, not only excluded the air, but kept the mass in constant agitation and prevented "bumping."

The precipitate thus forms in a granular condition excellently well adapted to bear without alteration the processes of washing and filtering which follow. It does not adhere to the tubes or sides of the flask, and unless there is some oxidizing agent in the solution it does not contain the least trace of free sulphur. The precipitate was washed with boiling water, and as it settles rapidly and quite

compactly it was easily washed in the same flask in which the solution was made and the precipitate formed. The precipitate usually occupied about one-tenth of the volume of the flask, and after drawing off the filtrate our rule was to fill the flask five times with boiling water. We were sometimes troubled by the breaking up of the precipitate and the washing of it through the filter, under such prolonged treatment. As is well known, this can easily be prevented by acidifying the wash water, however slightly, with hydrochloric acid, or by an excess of H_2S; but as the last was liable to oxidation, and the first still more objectionable, for reasons which will soon appear, we employed for the same purpose a solution of carbonic dioxide, and this, as we found, effectually prevented the disintegration. If by not settling promptly the precipitate showed any signs of breaking up, we passed a current of CO_2 through the hot water before it was used in the last one or two washings.

In all the later determinations we collected and dried the precipitate in a large platinum crucible by the method of reverse filtering illustrated and described at length on page 124 of the previous volume of these "Proceedings." But, in the two determinations made by the method just described, the precipitate was collected and dried on the porous earthenware filtering cones described by Prof. C. E. Munroe.* The cones with the precipitate were first dried at 100°, and then heated to 220° C. in an atmosphere of carbonic dioxide. Between 210° and 220°, depending somewhat on its condition, the red sulphide of antimony changes suddenly into the gray modification, and in this last condition the product was weighed. In each of these two determinations, on dissolving the gray sulphide in boiling hydrochloric acid, out of contact with the air, a considerable quantity of black residue was obtained. This contained only a very small amount of free sulphur, but consisted chiefly † of carbon, resulting from the charring of the small quantity of tartaric acid, which, as we find, sulphide of antimony invariably carries down with it when precipitated under the conditions here described, and which cannot be removed by any amount of subsequent washing. This charring takes place at the moment when the red is converted into the gray sulphide, and is undoubtedly caused by the heat evolved

* American Journal of Science, May, 1871.

† In our preliminary experiments, traces of both lead and copper appeared in this residue, which we traced at once to the tartaric acid "*purissimum*" used, and we found it impossible to procure from chemical dealers tartaric acid free from these impurities. We were obliged, therefore, to purify ourselves all the acid we employed.

during this process. That at this point the charring is perfect, and that after the conversion no tartaric acid is left undecomposed, we have proved by several times heating the resulting gray sulphide to 300°, and ascertaining that it underwent no additional loss of weight. As is well known, small quantities of tartaric acid are completely decomposed at this last temperature.* In the two determinations we are discussing, the carbonaceous residue was collected on a weighed filter, and its weight subtracted from the total weight of the dried precipitate. All the remainder was pure Sb_2S_3; and, from its weight and that of the antimony used, the ratio between the atomic weight of sulphur and that of antimony was very easily calculated. The results were as follows:—

FIRST DETERMINATION.

Weight of antimony taken	2.0554	grammes.
Weight of precipitate dried at 240° . .	2.8878	"
" carbonaceous residue. . . .	.0147	"
" Sb_2S_3	2.8731	"
" antimony as above	2.0554	"
Corresponding weight of sulphur . . .	0.8177	"
Hence when S = 32, then Sb = . .	120.6	"

SECOND DETERMINATION.

Weight of antimony taken	2.0346	grammes.
Weight of precipitate dried at 240° . .	2.8513	"
" carbonaceous residue . . .	0.0073	"
" Sb_2S_3	2.8440	"
" antimony as above	2.0346	"
Corresponding weight of sulphur . . .	0.8094	"
Hence when S = 32, then Sb = . .	120.6	"

It is evident that these results, so far as they go, very greatly tend to confirm the value Sb = 120.3 obtained by Schneider; and, in the light of the knowledge we have since obtained, the reason that our first

* Gmelin's Handbook of Chemistry, Cavendish Edition, vol. x. p. 209.

results were somewhat higher than his is perfectly evident. Whenever sulphide of antimony is precipitated under the conditions we have described, it always carries down with it, not only a small amount of tartaric acid, but also a very appreciable quantity of oxichloride of antimony, SbOCl, which, like the impurity first named, cannot be removed by washing the precipitate. The molecular weight of SbOCl (171.5) differs but slightly from the *equivalent* weight of Sb_2S_3 (168), so that, were the precipitate dried at 100°, a small admixture of this compound would not sensibly affect the total weight. But, as soon as the temperature reaches 170°, this oxichloride begins to be decomposed, $SbCl_3$ volatilizes, and the more stable oxichloride $Sb_4O_5Cl_2$ is formed. At a low red heat, this last compound is also in its turn decomposed, still more $SbCl_3$ escapes in vapor, and the final residue is antimonious oxide in a crystalline condition. These changes may be represented thus: —

$$\text{1st.} \quad 5\ SbOCl = Sb_4O_5Cl_2 + SbCl_3.$$

$$\text{2d.} \quad 3\ Sb_4O_5Cl_2 = 5\ Sb_2O_3 + 2\ SbCl_3.$$

At least, these are the reactions when SbOCl is heated by itself in an atmosphere of CO_2, as we shall show further on in this paper. In the presence of a large mass of Sb_2S_3, containing also a trace of organic matter, these effects are undoubtedly somewhat modified and have not been exactly traced. But whenever a precipitate of Sb_2S_3 formed as we have described is heated much above 150°, it yields a white sublimate; and this sublimate, which we have repeatedly tested, consists chiefly of antimony. At times it was pure chloride of antimony which crystallized on the walls of the glass tube used in the experiment; but, when very small in amount, the sublimate was an amorphous white powder, which appeared like oxichloride of antimony, and which may have been formed by the action of a minute quantity of chloride of antimony on the products of the decomposition of the equally small amount of tartaric acid also occluded by the precipitate. It has long been known that precipitated sulphide of antimony dried at 100° loses weight when heated to a higher temperature, and it has generally been assumed that this loss was due to hygroscopic water. But red sulphide of antimony, when precipitated as we have described, is not in the least hygroscopic and can be dried perfectly at 100°. At least, we have never been able to obtain evidence that, after being thoroughly dried at this temperature, it ever contains water as such; and we are confident that the loss of weight is due solely to the causes

we have assigned. At the time the first two determinations were made, these facts were not known, and no allowance was made for the loss of chloride of antimony which must have been incurred. This loss fully accounts for the difference between the value we obtained, 120.6, and 120.3, that of Schneider.

It was at this stage of the investigation that we presented a preliminary notice of our results to the American Academy of Arts and Sciences, at the meeting of June 10, 1873. After this, the work was interrupted for more than two years, and was not resumed until the autumn of 1875. Meanwhile, we had perfected the process of reverse filtering above referred to, and devised a more certain, although indirect method of bringing into solution, in its lower condition of quantivalence, a known weight of antimony. This last consisted, firstly, in dissolving a weighed portion of antimony in hydrochloric acid with the least possible addition of nitric acid; secondly, in reducing the solution thus obtained, by boiling it over bullets of pure antimony, determining from the loss of weight of the bullets the amount of metal dissolved. Evidently, the mass originally taken, plus the amount dissolved from the bullets, gave the weight of antimony used in each determination. Several important facts were observed in connection with each of these steps.

1st. It is usually stated that antimony is only very slightly acted on by pure hydrochloric acid, even when concentrated and boiling, but that it readily dissolves on the addition of only a very small amount of nitric acid.* We found that, when wholly protected from the air or oxidizing agents, pure antimony not only does not decompose pure hydrochloric acid, but also that in contact with the air the smallest amount of nitric acid will determine the solution of an indefinite amount of the metal. Assuming that the product of the reduction of the nitric acid is wholly NO, and therefore that the smallest amount theoretically required for the reaction would be represented by the expression, —

$$Sb + (3HCl + HNO_3 + Aq) = (SbCl_3 + 2\ H_2O + Aq) + NO,$$

then 40 parts of antimony would require, in addition to an abundant supply of hydrochloric acid, 21 parts of HNO_3 for its complete solution. The pure nitric acid which we used had a specific gravity of 1.355, and contained therefore about 54% of HNO_3. The same acid diluted with nine times its volume of water, to form what we will call

* Author's Chemical Philosophy, p. 265.

the decim acid, contains only 5.4% of HNO_3; and hence one gramme of antimony, according to our reaction, ought not to dissolve, if less than 10 cubic centimetres of this decim acid were used. Now, in one experiment, of which we have the details on record, 5 grammes of finely powdered antimony were treated in an open flask with 50 cubic centimetres of strong and pure hydrochloric acid, and to this only 1 cubic centimetre of the decim acid was added. The flask was placed in a warm place (30° C.), and frequently shaken. After a short time, the acid became colored reddish-yellow, and the chemical action began. As soon as it ceased, the materials in the flask were shaken together, when the solution became as colorless as water. But on standing in the air the color rapidly returned, and we observed that it always spread from the surface of the liquid downwards. These phenomena were repeated again and again, until after many days the whole of the antimony dissolved. According to our reaction, the 5 grammes of metal should have required 50 cubic centimetres of acid, so that the effect was obtained with only one-fiftieth of the amount indicated by this theory. The action is probably due to the NO, which remains in solution, and in conjunction with the oxygen of the air decomposes the hydrochloric acid, perhaps thus, —

$$2\,NO + 4\,HCl + O_2 = 2\,NOCl_2 + 2\,H_2O,$$

then

$$Sb_2 + 3\,NOCl_2 = 2\,SbCl_3 + 3\,NO;$$

and afterwards these reactions are repeated indefinitely. But, whether they represent the precise order of the chemical changes or not, there is no question that here, as in the complex reactions of the sulphuric acid chambers, the nitric acid or its products acts as a carrier, and that the oxygen which combines with the hydrogen of the hydrochloric acid comes chiefly from the atmosphere. In practice, we usually used, for dissolving 2 grammes of antimony, 30 cubic centimetres of strong hydrochloric acid and 5 cubic centimetres of the decim nitric acid; and, although this is only one-fourth of the amount of nitric acid required by the formula generally accepted, it is sufficient to determine a very energetic chemical action, during which a large part of the nitric oxide escapes. The action does not generally come on for some time (fifteen or twenty minutes), although it can be hastened by placing the flask in a warm place. But otherwise we did not heat the acid until almost the whole of the antimony was dissolved. When only a few centigrammes of metal remained undissolved, we connected the flask with a reversed Liebig's condenser and raised the contents to

the boiling point. The effect of this was to arrest the chemical action by driving off the nitric oxide; and, if the point was rightly chosen, the small residue of antimony, in passing into solution, would reduce almost all of the higher chloride of antimony which had been previously formed. We found it better, however, that some of the higher chloride should be left unreduced rather than that the least trace of antimony should remain undissolved. In the last case, it was necessary to add additional nitric acid, which made trouble at the next stage of the process; and the fact repeatedly observed, that under these circumstances a few milligrammes of antimony will not dissolve in a large excess of hydrochloric acid, even after prolonged boiling, is a sufficient proof of the statement made above,—that pure antimony will not decompose pure hydrochloric acid, unless some oxidizing agent is also present.

2d. Having thus brought a weighed amount of antimony into solution, so that almost the whole was in the condition of antimonious chloride, we completed the reduction by boiling the acid solution over bullets of pure antimony. These bullets were cast in a bullet-mould, and afterwards turned in a lathe, so as to secure a perfectly clean, smooth, and compact surface. Two or three of them were next weighed together in a platinum tunnel, supported vertically by a light glass stand, on the pan of the balance. From the tunnel they were transferred one by one, without touching with the fingers, to the flask containing the solution of antimony made as just described. The flask was then again connected with the reverse condenser, and the liquid boiled; while through a second opening in the cork a slow current of carbonic dioxide was caused to flow through the apparatus. The boiling was continued until the reduction was complete, and the point was indicated by the circumstance that, when it is reached, the solution, at first having a light straw color, becomes perfectly colorless. The original color is caused by the presence of an exceedingly minute amount of iron, which it is almost impossible to keep out of the solution. Indeed, the very dust of the atmosphere will impart enough for the purpose; and this color under these conditions is as delicate a test for iron as that caused by potassic sulphocyanide. It served here as a very useful indicator, but it was no sign whatever of any appreciable amount of impurity, either in the metal or the acid. Another indicator which can be used, although not nearly so conveniently, is the well-known solution of potassic iodide in starch paste, the acid solution of chloride of antimony giving with this reagent the familiar blue color before, but not after, it has been reduced.

It has long been known that the vapor from a boiling solution of antimony in hydrochloric acid carries off a portion of the chloride of antimony. We have found that this is true only when the solution is quite concentrated: that the amount which escapes rapidly diminishes as the solution is diluted, and that it soon becomes wholly imperceptible. Still, as in our experiments the boiling was frequently greatly prolonged, we guarded against any loss from this cause by using the reversed condenser, as above described. The time required for the reduction varied very greatly under different conditions. It was seldom finished in less than an hour, and the process frequently required several hours. The boiling was stopped as soon as the pale color of the solution was perfectly discharged; but, while the flask was cooling, the current of carbonic dioxide was steadily maintained. When cold, a measured portion of a concentrated solution of tartaric acid (containing generally from ten to fifteen grammes of the crystallized acid) was added to the flask, and the contents were then at once transferred to the large Erlenmeyer flask in which the antimony was to be precipitated. The transfer was accomplished very easily and perfectly in the following way.

Into the Erlenmeyer flask was first poured about 500 cubic centimetres of water strongly charged with carbonic dioxide; and then the platinum tunnel, on which, as we have stated, the antimony bullets had been weighed, and which had been carefully protected meanwhile, was placed in the mouth of the large flask. As the solution was now poured in from the smaller vessel, the bullets were of course caught by the tunnel, and the aërated wash water, which also passed through the tunnel, served to wash the bullets as well as the glass. The tunnel and its contents were then dried and weighed, and the loss from the previous weight gave accurately the amount of additional metal which had passed into solution during the process of reduction. It will be noticed that, during the whole process, the balls were never touched with the fingers, or brought in contact with any object by which their weight could be in the least altered. It was found however, to be essential to the success of the method that not more than a few decigrammes of metal, at most, should be dissolved from the balls; for, otherwise, the surfaces became disintegrated, and liable to abrasion. Hence, the objection to using an excess of nitric acid in dissolving the original quantity of antimony.

The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air, — fully as rapidly as the

solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air, if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grammes of antimony.

The method of precipitating the antimony after the solution was thus prepared has already been described (page 14). It is important, however, to add a few additional facts, which we observed in regard to the two impurities which the precipitated sulphide of antimony occludes; namely, tartaric acid and oxichloride of antimony. In the first place, we found that the relative amounts of these occlusions might be varied indefinitely by changing the relative proportions of tartaric and hydrochloric acids in the solution in which the precipitate was formed. As is well known, the antimony cannot be kept in solution without a certain excess of one or of both of these reagents. In proportion as the amount of one is diminished, that of the other must be increased; and we made a series of experiments to determine what were the minimum quantities required under different conditions. We made determinations in which the antimony was held in solution by hydrochloric acid only; and we found that, in that case, as much as one part of strong acid was required to five parts of water. We thus, of course, wholly avoided the occlusion of tartaric acid; but the amount of oxichloride carried down was so great that the results were worthless. On the other hand, in some more recent analyses, in which we began with pure chloride of antimony, we used only tartaric acid, and, in this case, although the carbonaceous residue was at times large, there was no loss by sublimation. Of the two occlusions, the tartaric acid is by far the least objectionable. This, as we have seen,* is wholly charred when the red sulphide of antimony is converted into the gray modifications, and the carbonaceous residue can be exactly estimated. In the case of the oxichloride of antimony,

* Page 15.

on the other hand, it is impossible to obtain any satisfactory control either over the chloride of antimony which escapes or the oxide which is left behind. Unfortunately, in starting from metallic antimony, we cannot avoid a large excess of hydrochloric acid in the solution, and must therefore expect more or less oxichloride of antimony in the precipitate. Assuming therefore that 15 cubic centimetres of strong hydrochloric acid were taken to dissolve every gramme of antimony, which was as little as could conveniently be used (but from this the greater part of the HCl gas was expelled during the subsequent boiling), it became, in the second place, an object to determine how much tartaric acid was required to hold the antimony in solution, and to reduce to a minimum the occlusion of oxichloride of antimony by the precipitated sulphide. With this view the following experiments were made. Four solutions were prepared by dissolving in each case 2 grammes of antimony in 30 cubic centimetres of hydrochloric acid, and reducing the solution as above described. To the first of these were added 5 grammes of tartaric acid, to the second 7 grammes, to the third 10 grammes, and to the fourth 20 grammes. They were then each diluted with water to one litre. In the first, oxichloride of antimony was precipitated at once. The other three remained clear; but, in the second and third, crystals of oxichloride formed on standing over night, and in the inverse proportion to the amount of tartaric acid added. On subsequently heating to boiling, the same crystals were precipitated even in the last, and the amount in the others very greatly increased. This crystalline precipitate formed as the solution was heated, and was deposited like acid tartrate of potassium wherever the glass rod touched the sides of the flask. From the first and second solutions almost the whole of the antimony was thus separated.

These crystals were analyzed, and found to be the oxichloride $Sb_4O_5Cl_2$. They will be described in a future paper. It is evident from these experiments that, under the conditions we have given,* from 5 to 10 grammes of tartaric acid to each gramme of antimony are required to prevent the formation of oxichloride of antimony, even in a cold solution; and our experience shows that, even with the larger amount, a perceptible although very small quantity of oxichloride is occluded by the precipitate formed with hydric sulphide. Moreover,

* In solutions of the same strength which have not been perfectly reduced, although containing but little of the higher chloride, the oxichloride does not appear to form nearly so readily; but we have made no quantitative experiments on this point.

our experience indicates that, with an intermediate amount, the loss and gain resulting from the causes we have mentioned are more or less closely balanced. By preserving as nearly as possible identical conditions, and taking, for example, to every 2 grammes of antimony 30 cubic centimetres of hydrochloric acid and 15 grammes of tartaric acid, it was found possible to obtain results closely agreeing not only with each other, but also with what we finally concluded was the most probable value of the atomic weight of antimony. But, during the investigation by which these facts were developed, we made many determinations with varying proportions both of hydrochloric and tartaric acid, in which the error arising from an excess of one or the other must have had its full effect. All these determinations not obviously defective are recorded below; and although a closer agreement would appear, were only those determinations selected which were made after the more accurate knowledge was obtained, and therefore under more favorable conditions, yet we feel much greater confidence in the result obtained by taking the mean of all, since in this mean the errors must be to a great extent, if not perfectly, balanced.

We were for some time in doubt in what condition the sulphide of antimony ought to be weighed, in order to obtain the most accurate results. Our final judgment was that the errors already referred to would best be balanced, while others would be avoided, by weighing the sulphide, after it had been dried, at from 180° to 200°, but before it was actually converted into the gray sulphide. This conversion takes place between 210° and 220°, varying to that extent in different cases. The change, as we infer, is attended with a sudden evolution of heat, and the action is quite violent. Small particles of the material are frequently projected from the vessel, and we sometimes noticed that the surface of the platinum nacelle became coated with the familiar sublimate of sulphide of antimony. If there was oxichloride in the precipitate, there may be an additional volatilization of chloride of antimony at this time; but the main loss, as we have constantly observed, takes place before the point of conversion is reached. We therefore concluded that more trustworthy results could be deduced from the weight of the red sulphide dried, as we have described, than from that of the gray; and, as will be seen, this judgment was fully confirmed by subsequent experiments on the haloid compounds. We have, however, in all but two instances weighed the sulphide in both conditions, and we give the results of both weighings; and on comparing these results in determinations 8 to 13 inclusive of the table on pages 36–7, which were made under the nearly identical conditions we have above indicated, it will be seen that the differences

are far smaller with the red sulphide than with the gray, which shows conclusively that additional causes of error must have affected the last weights, — another circumstance which sustains our judgment.

In the first twelve determinations we did not estimate the amount of the carbonaceous residue, which is assumed to be balanced by the loss of chloride of antimony, although we always tested the purity of the sulphide of antimony by dissolving it in hydrochloric acid, as described. In determination numbered 13, by some chance concurrence of favorable conditions, we succeeded in precipitating the antimony without the usual occlusion of oxichloride, although we used a large excess of hydrochloric as well as of tartaric acid. In this case, there was no evidence of sublimation nor loss during conversion, but a proportionally large carbonaceous residue, which was deducted from the weight of the sulphide; and the result of this determination, as will be seen, still further corroborates our conclusion. The same is true of some analyses of chloride of antimony made more recently, in which we dissolved crystallized chloride of antimony in a concentrated aqueous solution of tartaric acid, without using any excess of hydrochloric acid. In these cases also, the drying of the precipitate, and the conversion from the red to the gray modification, were attended with no appearance of sublimation. Were we to repeat the investigation with our present knowledge, we should follow the indications of these last analyses; and instead of attempting to make the two chief errors as small as possible, and balance them, we should seek to remove from the solution all the free hydrochloric acid, and thus eliminate the error due to the occlusion of oxichloride.* It would then, of course, be necessary to determine in all cases the carbonaceous residue, which might however be very large, without impairing the accuracy of the result. Still, our experience with these antimony determinations would lead us to fear that we might thus raise up as many hindrances as we avoided, and the determination we have given as No. 13 is sufficient for all purposes of comparison.

Before giving the results, it only remains to describe the manner in which the precipitates were dried, tested, and weighed. After that, by the method of reverse filtering, the precipitate had been washed, and collected in a large platinum crucible, as described on pages 14 and 15 of this article, it was dried in an air bath, at a temperature

* Our experiments also indicate that, even in presence of a large excess of hydrochloric acid, the occlusion of oxichloride can be prevented by using a very large excess of tartaric acid. It was under these conditions that the determination No. 13 was made. Of course, the occlusion of tartaric acid is then large; but, as shown, this need not impair the accuracy of the result.

varying from 100° to 130° C. in different cases; and, with time enough, the lower temperature seemed to be equally effective. Thus in one case we have the following weights recorded: —

Weight of Sb_2S_3 dried in a steam-chest . . .	2.1700	grammes.
„ same after 30 minutes at 150° . .	2.1685	„
„ „ „ additional .	2.1685	„
„ „ conversion at 210° . .	2.1677	„

By drying, as is well known, the precipitate shrinks to a very small volume. A small portion was then taken and dissolved in hydrochloric acid, in order that we might be sure no free sulphur was present; but so effectual were the precautions against oxidation we have described, that after our process was perfected we obtained in no case the least trace of residue. The larger part of the dried precipitate was next transferred to a platinum nacelle; and, the weight of this portion having been exactly determined, the nacelle was introduced into a glass tube about three-fourths of an inch in diameter. The portion of the tube holding the nacelle was heated by an air bath, through which the tube passed and was tightly held. This air bath was made of sheet iron. It had a double bottom, and a tubulature on one side for a thermometer. The cover consisted of a thin sheet of mica, through which the nacelle could be seen within the tube, and every change accurately observed. The bath was heated by a common gas burner, and the temperature regulated by regulating the flow and pressure of the gas. During the heating, a slow current of hydrogen was passed through the tube. This gas, made from oil of vitriol, zinc, and water, in a large germinator, was first purified by passing through solutions of caustic potash and nitrate of silver, and afterwards dried by sulphuric acid and chloride of calcium. The gas entered and passed out through tightly fitting corks, and the glass exit tube was made small in order that the least condensation of moisture on its walls might be the more apparent.* In this simple apparatus, the dried precipitate was maintained at a temperature between 180° and 200°, until the weight was constant. The nacelle was then again returned to the tube and heated to 210°, or until the conversion of the red sulphide of antimony into the gray modification took place, and the weight again

* The apparatus is the same as that subsequently used for the sublimation of bromide and iodide of antimony, and figured on page 57, with this exception, that the large adapter which there serves as a receiver is replaced by a small glass tube, as described above.

taken. Lastly, from the loss of weight thus observed, the correction to be subtracted from the first weight of the whole precipitate was easily calculated. It is evident that with this apparatus we were enabled to collect and examine the products sublimed during the heating, and form a very accurate estimate of the relative amounts under different conditions; and it was from the phenomena thus observed that we deduced the inferences which have already been stated. One or two additional remarks, though in part a repetition, are here important.

1. Although, during the course of the investigation, the experiment was repeated a great number of times, yet in no case, even when the precipitate was dried at 100°, was there the least deposition of water on the walls of the exit tube. Were there as much hygroscopic water present as has been usually supposed, it must have shown itself under these circumstances. Of course, a very minute amount would escape detection, and we sought to obtain more positive evidence, both by means of dried sulphate of copper and also by a chloride of calcium tube; but the evidence of the first was wholly negative, and from the slight and irregular variations of the last no positive indications could be drawn. In some cases, the weight of the chloride of calcium tube was obviously affected by the vapor of chloride of antimony; while in other cases, as in the example cited on page 25, the accidental variations in the weight of the tube were greater than the quantity, if any, we sought to estimate. During the charring of the occluded tartaric acid, of course some water must be formed, and the decomposition was made very evident by the familiar empyreumatic odor, which was always plainly perceptible; but the action was too complex and irregular, and the amount of the products too small, to admit of any trustworthy estimates by the usual methods.

2. The change of sulphide of antimony from the red to the gray modification is very sudden and striking. The temperature at which it takes place varies between 210° and 220°, depending on conditions which we could not wholly trace. It begins at some one point, and then spreads very rapidly through the mass. During the change, as has been stated, small particles of the material are sometimes projected from the nacelle; and there is not unfrequently evidence that at some points of the mass the temperature must have risen high enough to volatilize the sulphide of antimony. Frequently also at this time an additional amount of white sublimate was formed, and the peculiar empyreumatic odor again perceived. Under these circumstances, there was always a decided loss of weight. But at other times, especially

when the precipitate contained no oxichloride of antimony and had been heated for several hours to a temperature near the point of conversion, the change was attended with no loss of weight which was appreciable, as, for example, in the experiments cited on page 25, and in the determination numbered 13 below. After conversion, as we found in several experiments, the gray sulphide may be heated to 250° or even 300° without further loss.

The change of condition just described is not attended, however, with any very marked amount of condensation. We made the following determinations of the specific gravity of the sulphide of antimony in the two conditions. The specimens were weighed in alcohol of known density, and the specific gravity referred to water by calculation. An air pump was used to remove any entangled air.

RED SULPHIDE OF ANTIMONY DRIED AT 180°.

1. Specific Gravity determined at 26°.7 = 4.226.
2. " " " " 23°. = 4.223.

GRAY SULPHIDE OF ANTIMONY* CONVERTED AT 210°.

1. Specific Gravity determined at 28° = 4.288.
2. " " " " 27° = 4.289.

The published determinations of the specific gravity of the native antimony glance give values varying between 4.52 and 4.75; and Heinrich Rose gives † for the specific gravity of the artificial product made by melting together the constituents the value 4.614, and for the same, after pulverizing, 4.641. He also gives for the precipitated sulphide the value 4.421. It is evident, therefore, that the value varies, but in the above determinations the comparison of the two modifications were made under as nearly as possible identical conditions. Possibly, the decomposition of the occluded tartaric acid, producing a more or less spongy condition in the mass, may be the cause of the observed differences.

In the later determinations, when for the reasons we have stated the occlusion of tartaric acid was large, the gray sulphide, after having been weighed, was always dissolved in hydrochloric acid, and the carbonaceous residue estimated. The solution, having been mixed with

* Same as obtained in determination of table, pages 36–7, No. 8.

† Poggendorff, Annalen, lxxxix. 122.

tartaric acid and diluted with water, was filtered, and the residue collected on one of the smallest paper disks used in the process of reverse filtering. The disk was then dried and reweighed. The constancy of weight with these paper disks was very remarkable; and it may give greater confidence in the accuracy of our method to add here a few comparisons of the weights of the larger-sized disks which were used in collecting the sulphide of antimony itself, taken before and after they had been used. The first column gives the original weight of the disks, which were first dried at 120°, and then kept in an atmosphere dried by sulphuric acid. The second column gives the weight of the same after it had been used in filtering, and taken from the crucible after the first weighing with some of the dried precipitate adhering. We have only one weight of this kind recorded; but this will show how little of the precipitate adheres to the filter. The third column gives the weight of the same paper disk, after washing first with sulphide of ammonium, then with water, and drying.

	I.	II.	III.
Experiment 1	0.0654 gram.	0.0686 gram.	0.0654 gram.
„ 2	0.0375 „		0.0377 „
„ 3	0.0457 „		0.0458 „
„ 4	0.0436 „		0.0437 „

It should here be noted that in regarding all the carbonaceous residue as extraneous matter, and subtracting its weight from the total weight of the precipitate, we leave all the causes of loss in our determinations unbalanced. We estimate as sulphide of antimony the material which bears a temperature of 300° unchanged, and dissolves in hydrochloric acid; and every known cause of error must tend to diminish the weight obtained.* But less sulphide of antimony corresponds to a higher apparent atomic weight of antimony; and hence, in those determinations in which the weight of the insoluble residue has been taken into account, the tendency of all the known errors must be to

* Besides the causes of loss we have mentioned, and the small mechanical losses incident to every process of the kind, we must not overlook the fact that under most conditions a precipitate of sulphide of antimony is slightly soluble in the surrounding menstruum, and in our determinations this was frequently indicated by a barely visible coloration of the filtrate. Moreover, in several instances, we observed in this filtrate a condition which is familiar in titrations of silver; namely, a state in which either a solution of antimony or a solution of hydric sulphide would strike a red coloration.

increase the apparent atomic weight, and, so far as our knowledge goes, it would seem impossible that the value obtained in 13 D., for example, should be too low. Moreover, the black residue is not always wholly carbon, and at times contains some antimony compound. Any siliceous or other insoluble material which accident had introduced into the analysis would of course be eliminated as a part of the residue; and the same would be true of all forms of organic matter, as well as tartaric acid, which the precipitate might absorb from the solutions in which it formed, or from the water by which it was washed.* It may be interesting, in this connection, to add a few determinations of the relative amount of combustible and incombustible matter in a few of these residues: —

No. 1.	Weight of residue	0.0067	grammes
	„ after ignition	0.0032	„
	Combustible	0.0035	„
No. 2.	Weight of residue	0.0078	„
	„ after ignition	0.0013	„
	Combustible portion	0.0065	„
No. 3.	Weight of residue	0.0064	„
	„ after ignition	0.0020	„
	Combustible portion	0.0044	„

Although this discussion of the causes of error was essential to the refinement of the process, it must not be inferred that the magnitude of these errors was proportional to the attention they have necessarily received, or that they are important except with reference to the accuracy required in the determination of an atomic weight. Except in those cases where, as has been stated, the amount was accurately determined and allowed for, the greatest possible error in either direction arising from occluded materials never exceeded a few thousandths of the weight estimated, and might safely have been neglected in an ordinary analysis. These errors, as we have stated, tend to balance each other; and their maximum effect is shown in the first two groups of determinations in the table on pages 36–7. In the group of five determinations 8–12, we endeavored, as has been stated, so to regulate the conditions that the opposite errors should balance each other; and the very remark-

* In one case, when no tartaric acid was used whatever, and when the antimony was kept in solution by hydrochloric acid only, as mentioned on page 22, we obtained a distinct carbonaceous residue, evidently from some organic material which the precipitate like a mordant had absorbed.

able agreement between these results and the mean of the first five is in itself a proof that we have been successful, and, moreover, their close agreement among themselves indicates that, so far as the mere mechanical details of the process are concerned, a perfection has been reached which will compare favorably with the most accurate methods of quantitative analysis. In order to exhibit the details of the work as far as practicable, we give below two examples of the most trustworthy determinations. The first is selected from the group 8–12, and is one in which no account is taken of the occluded material, but where it is believed that the conditions were so regulated that the two chief sources of error must on the average (not, however, necessarily in every determination) balance each other. This example is selected, because, although no account was taken of the carbonaceous residue, it was determined and examined, and thus some data are given for judging not only how large the errors were, but also how nearly they were balanced. The second example is unique. In this case, by a fortuitous concurrence of conditions, there was no oxichloride formed even in a solution containing an excess of hydrochloric acid, and no material sublimation of any antimony product. Here, then, we have fortunately a determination belonging to the same class as the others, in which the error is known to be all on one side, and where the error can be corrected by determining the carbonaceous residue. Since, moreover, in the details of its execution, this determination was faultless in every respect, the result it furnishes is of very great value as a standard of comparison. And, further, since the tendency of every known error not corrected by subtracting the carbonaceous residue is in the opposite direction, it seems impossible, at least, with our present knowledge, that the atomic weight of antimony should be greater than the value thus obtained.

Details of Determination marked No. 11 E.

The finely pulverized antimony was weighed in a platinum nacelle. By means of a loop of platinum wire, this nacelle was lowered into a glass flask having a capacity of about 150 cubic centimetres. The powder having been shaken out, the nacelle was withdrawn, replaced on the balance pan, and weighed.

Weight of nacelle and antimony . . .	8.2655	grammes.
" " "	6.2617	"
Weight of antimony transferred to flask .	2.0038	"

The antimony was next dissolved without the aid of heat in 30 cubic centimetres of hydrochloric acid mixed with 5 cubic centimetres of decim-nitric acid. Before complete solution had taken place, the flask was connected with a reversed condenser, and the solution boiled until every trace of the metal had disappeared. Next, the antimony bullets, previously prepared as described, were added, and the boiling continued until the solution was perfectly colorless. To this solution, after cooling, was added 20 grammes of tartaric acid, dissolved in about twice its own weight of water, and the solution transferred, in the manner before described, to an Erlenmeyer flask holding about two litres.

First weight of platinum tunnel and antimony bullets,	96.8646	grammes.
Second " " " " " " "	96.5267	"
Weight of antimony dissolved during reduction .	0.3379	"
" " " as above	2.0038	"
Total weight of antimony taken	2.3417	"

The surfaces of the bullets were not disintegrated, and there was no appearance of any antimony powder arising therefrom. After precipitation, at the ordinary temperature, the precipitate was gently digested for some time with a large excess of $H_2S + Aq$ before heating the liquid to the boiling point. Every detail was successful. The precipitate was washed six times, and collected as usual by reverse filtering in a large platinum crucible, and dried in air bath at from 120° to 130° C.

Weight of small paper disk	0.0388	grammes.
" " large platinum crucible . .	180.8345	"
	180.8733	"
Weight of crucible, filter, and Sb_2S_3 .	184.1580	"
Weight of red Sb_2S_3, dried at 130° . .	3.2847	"

A portion of the dried precipitate was dissolved in hydrochloric acid. It gave no residue. The rest was then transferred to a platinum nacelle, and heated, as has been described, in a current of pure and dry hydrogen gas.

Weight of platinum nacelle	6.2616	grammes.
" " " " and Sb_2S_3	9.0480	"
Weight of Sb_2S_3 transferred	2.7864	"

Weight after heating to 175° for half an hour . .	9.0433 grammes.
" " " " " half an hour longer .	9.0433 "
Loss at this temperature	0.0047 "
Loss calculated for whole amount of Sb_2S_3 . . .	0.0055 "
Weight after heating to 210°, and converting to gray modification	9.0430 grammes.
Total loss after conversion	0.0050 "
Loss calculated for whole amount of Sb_2S_3 . . .	0.0059 "

At 175° we observed a distinct sublimate, and at 210° a slight addition to it.

Weight of red Sb_2S_3, as above	3.2847 grammes.
Loss when dried at 175°	0.0055 "
Corrected weight of red Sb_2S_3	3.2792 "
Weight of antimony taken	2.3417 "
Weight of sulphur in combination . .	0.9375 "

0.9375 : 2.3417 = 48 : 119.90, resulting value of Sb.

Weight of red Sb_2S_3, as before	3.2847 grammes.
Loss when dried at 210°, and converted .	0.0059 "
Corrected weight of gray sulphide . .	3.2788 "
Weight of antimony taken	2.3417 "
Weight of sulphur in combination . . .	0.9371 "

0.9371 : 2.3417 = 48 : 119.94, the resulting value of Sb.

During the drying and conversion of the precipitate, there was a distinct empyreumatic odor, and on dissolving the gray sulphide in hydrochloric acid a considerable amount of black residue. This residue was collected on a weighed disk of paper, and examined.

Weight of carbonaceous residue calculated for whole precipitate	0.0078 grammes.
Weight of incombustible portion	0.0013 "
" " combustible portion	0.0065 "

Here the antimonial sublimate was but small, and the carbonaceous residue was evidently the preponderating cause of error. Hence, a result decidedly below the average. But, even if we subtract the whole of the combustible portion of this residue and leave the opposite errors uncompensated, we only raise the resulting value to 120.78.

Details of Determination marked 13 D.

Weight of nacelle and antimony . . .	8.2578	grammes.
" " "	6.2522	"
Weight of antimony transferred to flask .	2.0056	"

The metal was dissolved with 30 cubic centimetres of hydrochloric acid and 5 cubic centimetres of decim-nitric acid, as in last example. But more tartaric acid, 25 grammes, was used, and in addition 20 cubic centimetres of hydrochloric acid were added to the water in the large flask before pouring in the solution through the platinum tunnel.

First weight of platinum tunnel and antimony bullets,	95.5825	grammes.
Second " " " " " " "	95.2038	"
Weight of antimony dissolved during reduction . .	0.3787	
" " " as above	2.0056	"
Total weight of antimony taken	2.3843	"

Here the same remarks apply as were made at the corresponding stage of the previous example.

Weight of small paper disk	0.0436	grammes.
" " large platinum crucible . .	180.8315	"
	180.8751	"
Weight of crucible, filter, and Sb_2S_3 .	184.2290	"
Weight of Sb_2S_3, dried at 130°	3.3539	"

Most of the precipitate was transferred to a platinum nacelle, and heated as before described.

Weight of platinum nacelle	6.2518	grammes.
" " " " and Sb_2S_3 .	9.4242	"
Weight of Sb_2S_3 transferred	3.1724	"

Weight after heating for some time at from 175° to 195°	9.4200	grammes.
Weight after conversion 210°	9.4200	„
Loss at either temperature	0.0042	„
Loss calculated for whole amount of Sb_2S_3	0.0044	„

Only a very faint sublimate was formed, but we noticed a very marked empyreumatic odor. We therefore infer that the loss of weight was caused wholly by the decomposition of the occluded tartaric acid, and on dissolving the gray sulphide in hydrochloric acid we obtained a large amount of carbonaceous residue, which was collected on a paper disk, and weighed.

Weight of paper disk, dried	0.0280	grammes.
„ „ „ „ and residue . . .	0.0400	„
„ „ residue	0.0120	„
Weight of residue calculated for whole amount of Sb_2S_3	0.0126	„

Hence we have —

Weight of Sb_2S_3 dried at 130°, as before		3.3539	grammes.
Loss on heating to 210° . . .	0.0044		
Carbonaceous residue	0.0126	0.0170	„
Estimated as pure Sb_2S_3		3.3369	„
Weight of antimony taken		2.3843	„
Weight of sulphur in combination . . .		0.9526	„

0 : 9526 : 2.3843 = 48 : 120.14, the resulting value of Sb, whether we take the red or the gray sulphide.

The above examples will illustrate how the results were obtained which are tabulated on pages 36–7.

SYNTHESIS OF

No.		Wt. in gram of Sb taken.	Wt. dissolved from balls.	Total weight of Sb used.	Wt. of red Sb_2S_3 dried at 180° C.
1.	A.	2.0036	0.2023	2.2059	3.0898
2.	E.	2.0017	0.2662	2.2679	3.1778
3.	E.	2.0113	0.0853	2.0966	2.9383
4.	A.	1.9973	0.0798	2.0771	2.9051
5.	E.	2.0019	0.1087	2.1106	2.9508
		Mean of 5 Determinations		....	....
6.	A.	1.7638	0.0430	1.8068	2.5301
7.	A.	2.0275	0.0894	2.1169	2.9639
8.	B.	2.0116	0.0188	2.0304	2.8423
9.	B.	2.0027	0.1000	2.1027	2.9429
10.	E.	2.0015	0.1424	2.1439	3.0025
11.	E.	2.0038	0.3379	2.3417	3.2792
12.	E.	2.0014	0.2168	2.2182	3.1061
		Mean of last 5 Determinations		....	....
13.	D.	2.0056	0.3787	2.3843	3.3369
		Mean of the 13 Determinations		....	....

* Large residue of carbon, small sublimate.
† Small residue of carbon, large sublimate.
‡ Weight of black sulphide not found.
§ Both residue and sublimate small.

SULPHIDE OF ANTIMONY.

Per cent of S in same.	Corresponding At. Wt. of Sb when S = 32.	Wt. of black Sb_2S_3 dried at 210° C.	Per cent of S in same.	Corresponding At. Wt. of Sb when S = 32.
28.61	119.79	3.0881	28.57	120.02*
28.63	119.64	3.1764	28.60	119.82*
28.65	119.56	2.9350	28.57	120.03*
28.50	120.41	2.9021	28.43	120.85†
28.47	120.57	2.9486	28.42	120.89†
28.572	119.994	....	28.518	120.322
28.59	119.91	....	....	....‡
28.57	119.97	....	....	....‡
28.57	120.04	2.8410	28.53	120.23§
28.55	120.13	2.9409	28.50	120.41§
28.58	119.94	2.9981	28.49	120.47§
28.59	119.90	3.2788	38.58	119.95§
28.59	119.92	3.1022	28.50	120.44§
28 576	119.986	....	28.520	120.298
28.55	120.14	3.3369	28.51	120.14 ‖
28.5731	119.994	....	28.522	120.295

‖ No sublimate or loss of weight on drying and conversion. Residue large, but weighed and subtracted. The best determination, and as perfect as can be made under conditions.

This point in our investigation was reached in the spring of 1876, and the results given above were presented to the American Academy of Arts and Sciences at their meeting of June 14th, 1876.* But although they agreed so closely with the results of Schneider, and although the close confirmation of his analysis thus furnished by our synthesis seemed so conclusive, yet we could not rest satisfied so long as the great discrepancy between this value of the atomic weight and the higher number obtained by Dumas remained unexplained. We therefore determined to repeat his experiments before publishing our results. Accordingly, in the autumn of 1876, we purified and analyzed a large number of different specimens of antimonious chloride, and the results are united in the following table. Beginning with crystallized chloride of antimony obtained from different dealers, and pure in a commercial sense, we first boiled for several hours the melted chloride over finely pulverized metallic antimony, using for the purpose a glass retort, so tilted that the condensed liquid flowed back into the body of the vessel. When boiled in this way, the surface of the vapor is marked by a very well-defined ring in the neck of the retort; and by regulating the lamp this ring can readily be maintained very near the mouth, so that, while all the chloride of antimony condenses and flows back, any more volatile admixtures will gradually escape. The retort having been brought into its normal position, the chloride of antimony was next distilled; and, rejecting the first and last eighth which came over, the rest of the product was redistilled over strips of metallic zinc, and so on three or four times, rejecting at each distillation the first and last of the product. The final distillate was then still further purified by repeated crystallizations from fusion. As the fused mass solidifies quite slowly (indicating a large loss of latent heat), it is easy to arrest the process at any point, and pour off the still liquid portion from the crystals which have formed. The last can then be remelted, and the process repeated, and so on indefinitely as long as the material lasts. In this way, from several kilogrammes of the commercial chloride we obtained the few grammes of beautifully clear and perfect crystals used in our analyses. In the fifth preparation, the crystals were obtained not by fusion, but by cooling a saturated solution of the previously distilled chloride in purified sulphide of carbon. Such a solution, saturated at the boiling point of sulphide of carbon, deposits the larger part of the chloride, when cooled to the ordinary temperature. Naturally, every precaution was taken during the course of these preparations to protect

* These Proceedings, vol. xii. p. 282.

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this exceedingly hygroscopic substance from contact with moist air, and all the transfers were made in a portable photographic developing chamber, the air of which was kept dry by dishes of sulphuric acid. The portions for analysis were transferred, in this chamber, to tightly fitting weighing tubes; and, after the weight was taken, they were dissolved in a concentrated aqueous solution of tartaric acid, using about 5 grammes of tartaric acid to each gramme of chloride of antimony. The solutions were then diluted, and precipitated with argentic nitrate, weighing out in each case the amount required, so that only the least possible excess of the reagent should be added. The precipitates were washed and collected by reverse filtering in platinum or porcelain crucibles, and dried in an air bath at temperatures varying from 110° to 120°. They were weighed with the small disk of paper used in this process, and the invariability of the weight of these paper disks was repeatedly tested. Also, in several instances after removing the filter, the argentic chloride was heated to incipient melting; but, as in no case was its weight thus altered, this additional precaution seemed unnecessary. In the determination numbered 17, an attempt was made to ascertain whether the presence of antimony in the tartaric acid solution appreciably influences the precipitation of argentic chloride. In this analysis, the antimony was first separated from the solution by H_2S; and, the excess of this reagent having been removed by warming the filtrate with a small amount of ferric nitrate, the chlorine was precipitated in the usual way. The result, as will be seen, agrees as nearly as could be expected with those obtained by at once precipitating the chlorine from the antimony solution; and it was not until some time subsequently that the causes of error referred to on page 5 were discovered.

The letters in the following table indicate different preparations, thus: —

a was made from a crystallized chloride of Veron and Fontaine, Paris, which was purified in the manner described above.

b was made from a crystallized chloride marked Rousseau Frères, Paris, purified as before.

c was the same as *b*, again distilled and crystallized.

d, the same as *c*, after ten additional distillations.

e, the same as *d*, again distilled below 100° in a current of dry hydrogen gas.

f was made with a crystallized chloride from Merck of Darmstadt, purified by repeated distillations and subsequent crystallizations from bisulphide of carbon, after first treating with chlorine as described beyond.

g, same as *f*, but in this determination the antimony was first precipitated from the solution.

Analysis of Antimonious Chloride.

Determination of Chlorine.

No.	$SbCl_3$. grammes.		AgCl. grammes.	% of Chlorine. Cl = 35.5. Ag = 108.	At. Wt. of Sb. Cl = 35.5
1 *a.*	1.5974	yielded	3.0124	46.653	121.78
2 *a.*	1.2533	"	2.3620	46.623	121.93
3 *a.*	0.8876	"	1.6754	46.696	121.57
4 *b.*	0.8336	"	1.5674	46.516	122.46
5 *b.*	0.5326	"	1.0021	46.546	122.30
6 *b.*	0.7270	"	1.3691	46.588	122.10
7 *c.*	1.2679	"	2.3883	46.599	122.04
8 *c.*	1.9422	"	3.6646	46.678	121.66
9 *c.*	1.7702	"	3.3384	46.655	121.77
10 *d.*	2.5030	"	4.7184	46.635	121.87
11 *d.*	2.1450	"	4.0410	46.616	121.96
12 *e.*	1.7697	"	3.3281	46.524	122.42
13 *e.*	2.3435	"	4.4157	46.613	121.98
14 *f.*	1.3686	"	2.5813	46.659	121.75
15 *f.*	1.8638	"	3.5146	46.650	121.79
16 *f.*	2.0300	"	3.8282	46.653	121.78
17 *g.*	2.4450	"	4.6086	46.630	121.89
	Mean value for all analyses			46.620	121.94
	Theory when Sb = 122			46.608	122.
	" " Sb = 120			47.020	120.

If in calculating the per cent of chlorine from the results of the above determinations we use the atomic weights for silver and chlorine obtained by Stas (namely, Cl = 35.457 and Ag = 107.93), these per cents will be in each case very nearly 0.020 lower, and we shall obtain for the mean value 46.600 instead of 46.620. Moreover, on this assumption the atomic weight of antimony, deduced from Dumas's analysis of the chloride, would be 121.95 instead of 122. Again, if we use Stas's value of the atomic weight of sulphur (S = 32.074) in calculating the atomic weight of antimony from our own results, on the synthesis of the sulphide, we should obtain 120.28 instead of 120; and, lastly, the values Sb = 120.28 and Cl = 35.457 give for the per cent of chlorine in antimonious chloride the value 46.931.

Here, then, is a most striking result; for these determinations confirm the value of the atomic weight of antimony obtained by Dumas as closely as did the previous determinations confirm that obtained by Schneider. Evidently, there was a large constant error in one case or the other. Moreover, it appeared improbable that in either case any error could arise in the chemical process employed: for, in the first instance, we had a synthesis by one method confirming an analysis by a wholly different method; and, in the second instance, the analytical process employed is regarded as one of the most accurate known to science, and we had apparently shown that its accuracy was not impaired under the peculiar conditions present. It appeared, therefore, reasonable to assume that the results did truly indicate both the actual proportion of antimony in the sulphide of antimony and of chlorine in the chloride of antimony analyzed, and to look for the cause of the discrepancy to some impurity in one or the other compound. We therefore next sought to determine how much sulphide of antimony could be obtained from a given weight of chloride of antimony, hoping that by thus bringing the relations of antimony to chlorine and sulphur into close comparison the source of the error might be indicated.

The precipitation of sulphide of antimony from a solution of the chloride in tartaric acid is made under conditions which are far more favorable to accurate results than those with which we were obliged to contend in our previous experiments. If the solution is diluted with water charged with carbonic dioxide, and if the precipitation is made in the way we have described,* we can avoid all excess of hydrochloric acid except that which is formed by the chemical reaction, and there is then no oxichloride of antimony formed, and no subsequent loss

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* See page 14.

of chloride of antimony on heating the red sulphide up to the point of its conversion to the gray modification. Moreover, less tartaric acid is required, — not more than 6 grammes to every gramme of chloride, — and consequently less is occluded by the precipitate, so that with care the carbonaceous residue can be reduced to an insignificant amount.

The following table exhibits the results of these antimony determinations, as well as the general result of the assumed complete analysis of antimonious chloride. The per cent of chlorine taken is the mean of the first thirteen determinations of the previous table, as these only had been made at the time the second table was drawn up, and it therefore exhibits the results exactly as they were presented to us at this stage of the investigation.

Analysis of Antimonious Chloride.

Determination of Antimony.

	$SbCl_3$ taken in grammes.	Sb_2S_3 obtained in grammes.	% of Antimony when Sb:S=120:32.*	% of Antimony if Sb:S=122:32.†
1 *b.*	3.8846	2.8973	53.275	53.525
2 *b.*	5.1317	3.8417	53.473	53.725
3 *b.*	4.4480	3.3201	53.316	53.567
4 *b.*	4.5506	3.4009	53.882	53.633
5 *b.*	4.8077	3.6072	53.593	53.845
6 *b.*	4.2774	3.1958	53.367	53.618
Mean of all Analyses			53.401	53.652

Mean Result of Complete Analysis.

Antimony, the mean of six determinations	53.401	53.652
Chlorine, " " thirteen "	46.611 ‡	46.611 ‡
	100.012	100.263

* Or assuming that $\frac{4}{5}$ of the gray sulphide is antimony, as deduced from actual synthesis.

† According to the generally accepted theory.

‡ When Cl=35.5 and Ag=108, according to Dumas.

As they at first presented themselves to us, these new results, so far from throwing light on the subject, only rendered the problem the more obscure and baffling. Towards interpreting them however, one point seemed evident; — that, however little value our own experiments and those of Schneider might have in fixing the atomic weight of antimony, they had at least established, beyond all doubt, the proportion of this element in the gray sulphide weighed in our antimony determinations. For if we assumed, as those experiments indicated, that five-sevenths of the gray sulphide was antimony, then the amounts of antimony and chlorine found in the analysis of antimonious chloride just made almost exactly supplemented each other; while on the other hand, if this material was, as generally believed, pure Sb_2S_3, in which $Sb : S = 122 : 32$, then our determinations of one or the other of these elements must be greatly erroneous, and the excess obtained far too great to be explained by any known or probable imperfections of our methods. Of course, although the gray sulphide might contain, on the average, five-sevenths of its weight of antimony, it was a possible supposition that it might also occlude a constant amount of some undiscovered impurity, leaving the proportion of the sulphur to the antimony that which the atomic weights 122 and 32 required; and, were it not for our previous experience, this would have been the most obvious explanation of the discrepancy. Indeed, the new facts led us to re-examine this material, and review our previous conclusions, but with the same result as before. We could discover no impurity except the small amount of carbonaceous material which was so well known and taken into the account, and in our later determination (as is shown by the example on page 69) even this had been reduced to so small an amount as to be wholly insignificant. It is very difficult in any such case to prove a negative, but in the present instance the following considerations appeared conclusive, which on account of their important bearing we in great part recapitulate, although the evidence was again reviewed at this time.

1. Such an impurity must be comparatively large in quantity, not less than several centigrammes in the amount of the gray sulphide usually weighed.

2. It must exist to an equal extent in both the native sulphide and the artificial product of our analytical process, for both contain the same percentage of antimony.

3. It must be derived from antimonious chloride, tartaric acid, hydric sulphide, and water, which were the only reagents used in the process, and from these in the purest condition they could be obtained.

4. It must be able to bear a temperature of 300°C. without alteration, for in our later determinations the sulphide was heated to this temperature.

5. It must be soluble in hydrochloric acid; for allowance was made for the impurity which remained undissolved when the sulphide was decomposed by this reagent.

Hence, it still appeared, as before, quite impossible that any such impurity could be present; but, in order to eliminate even more certainly any unforeseen and accidental conditions, we made the following experiments.

In the first place, we brought together the aqueous solutions of hydrochloric acid, tartaric acid, and sulphide of hydrogen in the same proportions, and under the same conditions in which they were used in our antimony determinations; but, although we made several trials, we obtained in no case the slightest precipitate.

In the second place, we heated a small amount of the tartaric acid used to 300° C., treating it exactly in the same way as the precipitated antimonious sulphide in our analytical processes; and we found that the small amount of carbonaceous residue obtained was wholly insoluble in hydrochloric acid.

It would evidently have been more satisfactory to be able to determine the amount of combined sulphur in the gray sulphide, and thus to prove that it exactly supplemented the antimony, as we had endeavored to do in the case of the antimonious chloride; but unfortunately we could devise no method which promised to be satisfactory. We were obliged therefore to rest on the negative evidence, and this seemed to exclude the most obvious explanation of our contradictory results. Of course, we could not reasonably entertain the question that the large excess which the analyses of table pages 40 and 42 presented, when calculated for $Sb = 122$, was due wholly to an overestimate of the chlorine, because the amount of chlorine was only that which this theory of the composition of $SbCl_3$ required; and, moreover, the constancy in the composition of the chloride, after it had been submitted to such various treatment, was surprisingly great, and served to exclude the idea of any error at all comparable with that which the excess in question would imply. We had found apparently that the composition remained sensibly constant, even after the successive distillation of what we had regarded as essentially pure material. We had distilled it in a current of perfectly dry hydrogen, at a temperature below 100°, and still obtained in the distillate the same composition as before. We now further made the four additional chlorine deter-

minations, Nos. 14 to 17, in the table on page 40. The material for these analyses was first purified by repeated distillations as before, first over powdered antimony and then over zinc. Through the melted chloride was then passed, for a short time, a current of dry chlorine gas, in order to make sure that no such thing as a subchloride of antimony, if it can exist, or particles of metallic antimony, could be present. The chloride was then again redistilled several times, and this product purified by ten or twelve repeated crystallizations from a solution in disulphide of carbon, the material being protected all the time as far as possible from contact with moist air. The few grammes of pure chloride thus obtained from more than a kilogramme of so-called pure commercial chloride of antimony were submitted to analysis, and, as will be noticed, the results were in complete accordance with those we had obtained before. Lastly, we found nearly the same result, with only the little loss that was to be expected, when the antimony was removed from the solution before precipitating the chlorine.

Now, it is evident that, if the sulphide of antimony we weighed is pure, we are forced, even by these last analyses, to the conclusion that the atomic weight of antimony must be very nearly at least 120, if that of sulphur is 32, although the singular discrepancy which our results presented served at the time to render the problem exceedingly puzzling. The facts indeed seemed to indicate that, while antimony combined with chlorine in the proportion of 122 to 3 times 35.5, it combined with sulphur in the proportion of 120 to $\frac{3}{2}$ times 32, or 122 to $\frac{3}{2}$ times 32.53; in other words, that the relation of the atomic weights of chlorine and sulphur was not as accepted 35.5 to 32, but 35.5 to 32.53. And, although, after the investigations of Dumas, Stas, Marignac, and others, it was clearly out of the question that these values should be in error to the extent indicated, yet, as we have seen, Stas had found for the atomic weight of sulphur 32.074, and the results of our synthesis of sulphide of antimony calculated on this basis would give for the atomic weight of antimony 120.28. Moreover, it appeared that when the analyses of antimonious chloride made by Dumas were recalculated with Stas's values of the atomic weights of chlorine and silver ($Cl = 35.457$, $Ag = 107.93$), they gave for the same atomic weight the number 121.95. This reduced the difference between the two determinations to 1.67, and it did not seem impossible that the whole discrepancy might result from the accumulation of a number of similar small errors. We were thus led to undertake a new comparison of the atomic weights of chlorine and sulphur, based on the precipitation of sulphide of silver, by the same process we had employed in precipitating sulphide of

antimony, not with any expectation of correcting the atomic weight of sulphur, but with a view possibly of verifying the higher value obtained by Stas, and more especially of still further testing the accuracy of our method of precipitating sulphides; as it was obvious that any hidden sources of error which could have impaired the accuracy of our antimony determinations might be expected to reappear in the experiments with silver, and then the well-established composition of sulphide of silver would help us to detect them.

We began these experiments by taking two adjacent portions of the same piece of pure silver foil, and, having dissolved each in nitric acid, we in the first place precipitated the silver from both solutions, as chloride, with the usual precautions. The argentic chloride from the first solution was washed, collected, and weighed as before described. That from the second solution, having been thoroughly washed by the process of reverse filtering, was redissolved in the same vessel with pure aqua-ammonia, and from this solution the silver was precipitated as sulphide by adding the supersaturated solution of hydric sulphide, using the same precautions with which we were familiar in the precipitation of sulphide of antimony. The sulphide became granular on boiling, and was readily washed and collected by the method of reverse filtering. We thus hoped to obtain a direct comparison of the atomic weights of chlorine and sulphur, not depending on the absolute purity of the metallic silver used, and moreover to obtain a confirmation or otherwise of the general accuracy of our method of determining sulphide of antimony; for it was obvious that the same causes of error were likely to inhere in two such similar processes. Hence, although such experiment would probably only confirm values already well established, such a confirmation would give us confidence in the accuracy of our previous work. But although the mechanical details of the process appeared perfect, and the results were not inconsistent with the accepted values of the weights under discussion, yet they were neither sufficiently sharp nor constant to answer the questions we had proposed, owing probably to some slight solvent action of the ammoniacal menstruum on the precipitated sulphide of silver. We were therefore led to modify the process by first preparing pure sulphide of silver by the method we have described, and then determining the relation of silver to sulphur by reducing weighed portions of this sulphide in a stream of hydrogen gas. This result, compared with the already well-known relation of silver to chlorine, — probably the most accurately determined of all the atomic ratios, — would give us the relation of sulphur to chlorine which we sought, and under essen-

tially the same conditions as before. As thus modified, the method gave exceedingly sharp results, and the whole course of the analytical process seemed favorable to extreme accuracy. The reduction of the sulphide takes place at a temperature far below the melting point of silver, — indeed, below a visible red-heat, — and the metal separates in a most beautiful fine filamentary condition, which very greatly facilitates the reducing action of the hydrogen gas. Here again, however, we encountered another of those unforeseen constant errors which have caused us so much perplexity and fruitless labor during the whole investigation; and we give in the following table a series of results which have no other value than as illustrating the remark we have before made, that no amount of accordance in the results of the same analytical process is a sufficient guarantee against errors of this class: —

Reduction of Argentic Sulphide.

First Series of Experiments at Full Red Heat.

No.	Weight of Ag_2S, taken in grammes.	Weight of S, or loss during reduction.	Corresponding At. Wt. of S when Ag = 108.
1, *a*.	1.3380	0.1749	32.48
2, *b*.	1.2089	0.1582	32.52
3, *c*.	2.6592	0.3476	32.48
4, *c*.	1.9419	0.2540	32.50
5, *d*.	3.2784	0.4283	32.47
6, *e*.	2.4036	0.3143	32.49
7, *f*.	2.8359	0.3711	32.52 *

Mean value	32.494
Extreme variation from mean	.026

The sulphide used in the first five determinations was prepared from washed chloride of silver, which was dissolved in pure aqua-ammonia and precipitated with $H_2S + Aq.$, as described above. The portions used in the last two determinations marked *e* and *f* were precipitated from

* In this determination, the reduced silver fused.

ammonio-argentic nitrate, prepared in the first case from metallic silver, and in the last case from crystallized nitrate of silver, with the least possible excess of ammonia. During the process, a current of CO_2 was passed through the solution, which was boiled with the precipitate until all odor of ammonia had disappeared, when violent bumping ensued. After having been collected and dried, the sulphide was heated, in the first case to 280°, and in the last case to 300°, in a current of CO_2. We observed no sublimate, and there was no loss of weight with either preparation. Of the preparation *d*, seven grammes were boiled with strong hydrochloric acid until completely converted into chloride, which was then tested for sulphur, but none could be detected. The products of the decomposition of several of the preparations were tested for ammonia, and other volatile bases which might possibly have been occluded by the precipitated sulphide. Ammonia was at first found in abundance, but this was soon traced to an impurity in the hydrogen used in the reduction; and after this source of error was removed not the smallest quantity of any such product could be detected. It will thus be seen that these very closely according results were obtained with seven different preparations, made in part by different processes; and, further, that we had the strongest evidence of the purity of the material used; and, lastly, that the perfect metathesis of the sulphide with hydrochloric acid, leaving no residue of either elementary substances, proved that the silver was united to the sulphur in atomic proportions. Nevertheless, all these determinations were in error, and the error arose in this way: —

The argentic sulphide, held by a porcelain nacelle in a porcelain tube heated by a gas furnace, was reduced in a current of hydrogen gas. The hydrogen was prepared in an automatic generator, from clippings of sheet zinc, common sulphuric acid, and water, in the usual way; but, before reaching the porcelain tube, passed through a very long series of purifiers and driers, containing in order quick lime, soda lye, solution of acetate of lead, solution of argentic nitrate, sulphuric acid, and chloride of calcium. The object we had chiefly in view was to remove from the gas any traces of arseniuretted hydrogen or similar compounds; and we felt assured of its purity in this respect, on finding that it formed no metallic mirror even after passing for several hours through a glass tube heated to redness, and caused no darkening of "lead paper" after very prolonged exposure. The reduction of the sulphide of silver was of course attended with the evolution of hydric sulphide, and the process was continued until no trace of this substance could be detected with "lead paper" in the gas

which escaped from the porcelain tube. It was evident from the first that, as already stated, the reduction could be at least nearly completed below visible redness; and, as we now know, argentic sulphide can be perfectly reduced at this low temperature, but in all the earlier determinations we found it necessary to raise the temperature at the end of the process to a full red heat, and continue the heating for several hours before the untarnished lead paper indicated that the evolution of hydric sulphide had ceased. We subsequently discovered that this effect was due to the presence of the finely divided silver, determining a reducing action of the hydrogen on certain impurities which the gas had contracted from the crude sulphuric acid, and which had escaped all the purifiers. These impurities contained both nitrogen and sulphur, and, when reduced by hydrogen in presence of the metallic silver, yielded both ammonia — to which we have already referred — and also the hydric sulphide which had misled us in regard to the completion of the reduction. On passing the gas through a glass tube containing platinum sponge, heated to low redness, the effect was still more marked; and, on placing this tube after the first alkaline purifier, the products just named were evolved in abundance, although previously, even at this point, the gas produced no effect on "lead paper." We thus traced the impurity back to the hydrogen generator, and were able to remove it by placing in the line of the purifiers a glass tube filled with platinum sponge, and heated by a combustion furnace. The tube was placed, as above described, after the alkaline purifier; and from this the gas was passed through several purifiers containing a solution of nitrate of silver, and through driers containing in part sodic hydrate and in part calcic chloride. Afterwards, the nitrate of silver in the purifiers was replaced by alkaline and acid solutions of potassic permanganate, as recommended by Schobig,* which were, at least, equally efficient. The crude acid used in the generator was found to contain an unusual amount of nitric acid, and the impurity contracted by the hydrogen was probably some volatile compound of oxygen nitrogen and sulphur, similar to that with which we are so familiar in the sulphuric acid chambers. Misled, as we have seen, by the indications of sulphur, we continued the reduction — in the experiments whose results have been given on page 47, — far longer and at a far higher temperature than was necessary; and the apparent increased value of the atomic weight obtained was due to a slight volatilization of the metallic silver. Except in one of the experiments, the temperature had never reached

* Jour. pr. Ch. (2), xiv. 289, Oct., 1876.

the melting point of silver; but, as soon as our suspicions were aroused, we detected a slight mirror near the open end of the reduction tube, which, when dissolved off with a few drops of nitric acid, and tested with hydrochloric acid, gave abundant evidence of what had taken place. And, by subsequent experiments in a stream of hydrogen gas, we found that, under the conditions present in our experiments, silver volatilized — very slightly, it is true, but markedly — at a temperature considerably below its melting point.

We have thus shown, first, that recently reduced silver exerts a catalytic action precisely similar to that of spongy platinum, although not so powerful; and, secondly, that under these conditions the silver slowly volatilizes, at a temperature considerably below its melting point. Whether the volatilization is increased by the catalytic action, or why, in our experiments, the loss should have been so constant in amount, we have had no opportunity to determine. It was only necessary at the time to establish the fact that the results were vitiated by this constant error, and we at once hastened to determine whether the sulphide could be perfectly reduced at a temperature below that at which silver volatilizes in a current of pure hydrogen. To this end, we made many experiments, carefully testing in each case the reduced silver for sulphur, and examining with the greatest care the interior surface of the porcelain tube for any evidence of volatilization. We thus found that, by regulating the temperature, sulphide of silver could be perfectly reduced at a low red heat, without giving any evidence of loss from this cause. The following determinations were made in this way: —

Reduction of Argentic Sulphide.

Second Series of Experiments at Low Red Heat.

No.	Wt. of Ag_2S, grammes.	Wt. of S by loss.	At. Wt. of S. Ag = 108.	At. Wt of S. Ag = 107.93.
1, *a*.	7.5411	0.9773	32.160	32.139
2, *a*.	5.0364	0.6524	32.143	32.122
3, *b*.	2.5815	0.3345	32.155	32.134
4, *c*.	2.6130	0.3387	32.168	32.147
5, *d*.	2.5724	0.3334	32.164	32.143
Mean value			32.158	32.137
Extreme variation from mean .			0.015	0.015

In this series, as in the last, the letters indicate different preparations. The two marked *a* and *b* were both made from washed chloride of silver, dissolved in pure aqua-ammonia; that marked *c* was made from pure nitrate of silver, first converted into ammonio-nitrate, with the least possible excess of ammonia; that marked *d* was precipitated directly from a dilute aqueous solution of the same argentic nitrate, without ammonia, and was therefore formed in an acid solution. They were all precipitated with a supersaturated solution of hydric sulphide, and during the precipitation and subsequent boiling a current of carbonic dioxide was passed through the liquid. After the material had been placed in the nacelle for reduction, it was heated to 300°, in a current of carbonic dioxide, before the weight was taken. These facts are stated, because, as will be seen, the close accordance of the results obtained furnishes the strongest evidence of the uniform purity of the material prepared in the several ways we have described, and gave us great confidence in the perfection of our new method of precipitating sulphides.

Stas obtained for the atomic weight of sulphur when $Ag = 107.93$ the value 32.074, and the mean of our results differs from his by only 0.063. How small this difference really is, is shown by the fact that even with the largest quantity of sulphide used, — which required a platinum nacelle 5 inches long by $1\frac{1}{8}$ inches wide to hold the spongiform* mass of reduced silver, — the difference in question only corresponds to $1\frac{7}{10}$ milligrammes in the weight estimated; and with the smaller quantities — which required the largest porcelain nacelle we could obtain — the difference only corresponds to about half a milligramme. Still, the process is sufficiently accurate to show even this difference; for the extreme variations from the mean value in the last series of results only corresponds for the larger quantities to $\frac{4}{10}$ of a milligramme, and for the smaller to $\frac{15}{100}$ of a milligramme of the quantity estimated. The difference, therefore, small as it is, evidently points to a constant error of some kind, which, as we suspect, is caused by a slight volatilization of silver, even at this comparatively low temperature, although we were unable to obtain any other evidence of it. Hence, the following two additional determinations may be of interest, in which the sulphide was reduced below a visible red heat, in a small platinum nacelle, heated in a tube of hard glass: —

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* The production of moss silver in this process is a most beautiful phenomenon, which has been described by Dr. Percy, "Metallurgy," I. 360, and more recently by Professor Liversidge, of the University of Sydney.

Reduction of Argentic Sulphide.

Third Series of Experiments, Temp. below Visible Redness.

No.	Wt. of Ag_2S. grammes.	Wt. of S. by loss.	At. Wt. of S. Ag = 108.	At. Wt. of S. Ag = 107.93.
1.	1.1357	0.1465	31.990	31.969
2.	1.2936	0.1670	32.010	31.990
	Mean value		32.000	31.980

We are sure that in these experiments no silver was lost, because the least trace of sublimate would have been visible on the glass. We cannot be so certain that a trace of sulphide did not remain unreduced; but we do feel confident that the true value of the atomic weight of sulphur — so far, at least, as it can be determined by the analysis of argentic sulphide — must lie between the limits which the two last series of experiments fix. This is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end.

While, therefore, this portion of our investigation was not wanting in interesting results, it did not help us to explain the discrepancy we had observed in our experiments on the atomic weight of antimony. We now felt, however, greater confidence in our synthesis of sulphide of antimony; for if the sulphide of silver we had analyzed was so pure there was every reason to believe that the sulphide of antimony prepared in the same way was equally pure, save only the small occlusions which were so well known, and had been taken into account. We were therefore now still more fully persuaded that the value 120, which we had obtained for the atomic weight of antimony, must be correct within a few tenths of a unit; and it seemed to us very clear that the constant error, which had so perplexed us, was to be looked for in the analyses of chloride of antimony. Moreover, it seemed probable to us at this time that we might obtain a clew to the hidden source of error by analyzing the bromide and iodide of antimony before continuing our experiments on the chloride, for the same influences would be likely to affect all these processes; yet it was reasonable to expect that they would act in varying degrees in the three cases, and that they might thus reveal their nature. We begin with our work on the bromide.

We prepared the bromide of antimony by adding in small portions at a time the pulverized metal to a strong solution of bromine in sulphide of carbon. The retort containing the solution was kept cool by

snow, and shaken after each addition until the action ceased. As soon as the color of bromine was discharged, the sulphide of carbon was distilled off over a water bath; and then, replacing the water bath with a gas lamp, the bromide of antimony was first boiled, and then distilled over the finely powdered antimony which had been added in excess. On account of the high boiling point of bromide of antimony, and the readiness with which its vapor condenses, it was found best in distilling to cover the body of the retort with a hood. The bromide thus prepared was purified by repeated distillations over pulverized antimony, as in the case of the chloride, and finally by crystallizing and recrystallizing several times from solution in purified sulphide of carbon. A warm saturated solution in sulphide of carbon deposits, when cooled to the freezing point, the greater part of the bromide of antimony in fine acicular crystals. These crystals were dried first with blotting-paper, and then *in vacuo* over sulphuric acid. The antimonious bromide thus purified by fractional distillation and crystallization was only a very small fraction of the first crude product. It was pure white, had a high silky lustre, and, when first made, was wholly destitute of odor. It was carefully examined for chlorine, iodine, and arsenic; but the delicate test which we possess for all three of these elements, so frequently associated with commercial antimony and bromine, failed to show the least trace of either in the bromide of antimony we analyzed. The determinations of bromine were made in all respects like those of chlorine. Great care was taken not to add more than a very slight excess of argentic nitrate, and we found that under these conditions the supernatant liquid cleared more readily above the precipitate in the case of bromide of silver than with the corresponding chloride, and for this reason the first could be washed more quickly than the last. The results of these determinations are embodied in the table on the following page.

Here, as before, the letters indicate different preparations: *a* was made and purified as described above; *b* was the same material as *a* redistilled and again crystallized from bisulphide of carbon; *c* was another portion of the same material several times redistilled and twice recrystallized from the same solvent; *d* was a separate preparation from the start; *e* was another separate preparation purified with extreme care. In the last case there was over a kilogramme of the crude product, which was reduced by the fractional distillation and crystallization — each process repeated from ten to twenty times — to the few grammes used in the analyses. These methods of purifying the substance were thus pushed to their utmost limits.

Analyses of Antimonious Bromide.

Determination of Bromine.

No.	Wt. of Sb Br_3 taken in grammes.	Wt. of Ag Br obtained.	% of Bromine. Br = 80, Ag 108.
1, *a*.	1.8621	2.9216	66.765
2, *a*.	0.9856	1.5422	66.584
3, *b*.	1.8650	2.9268	66.779
4, *b*.	1.5330	2.4030	66.703
5, *b*.	1.3689	2.1445	66.663
6, *c*.	1.2124	1.8991	66.655
7, *c*.	0.9417	1.4749	66.647
8, *d*.	2.5404	3.9755	66.593
9, *d*.	1.5269	2.3905	66.623
10, *e*.	1.8604	2.9180	66.743
11, *e*.	1.7298	2.7083	66.624
12, *e*.	3.2838	5.1398	66.604
13, *e*.	2.3589	3.6959	66.671
14, *e*.	1.3323	2.0863	66.635
15, *e*.	2.6974	4.2285	66.708

Mean value from last six determinations . 66.664

Mean value from all the determinations . 66.6665

Theory Sb 120 requires 66.6666

Theory Sb 122 „ 66.2983

If in calculating the results of the above bromine determinations we use the atomic weights of Stas, — Br = 79.952, Ag = 107.93, — the per cents found will be in each case only 0.002 higher, which is, of course, an inappreciable difference. Hence, whether we take Stas's or Dumas's values for the atomic weights of bromine and silver, the atomic weight of antimony deduced from the above determinations is exactly 120.00.

This is certainly a remarkably close confirmation of our previous conclusion. Indeed the wonderful coincidence between the observed and the theoretical results must be to a certain extent accidental; for no process of chemical analysis is capable of the accuracy which this agreement would imply. Still it should be noticed that the probable errors of the process, so far as they are indicated by the variations from the mean value, are not larger than we might expect would be eliminated by multiplying observations; and, further, that the mean of the last six determinations which are undoubtedly the most trustworthy, is nearly as close to the theory as the mean of the whole.

But not only did these experiments on bromide of antimony thus confirm our previous conclusion: they also gave the first definite clew to the explanation of the disagreement with otherwise consistent results which our experiments on chloride of antimony had presented. The one difference between the chloride and the bromide, which appeared to render the last better suited to yield accurate results, was the difference in their hygroscopic qualities. As we have stated, the chloride is one of the most hygroscopic substances known. The bromide is also hygroscopic, but far less so, presenting no unusual difficulties of manipulation; and, since our tests indicated that both substances were otherwise pure, we at once drew the inference that the different results we had obtained with chloride of antimony must depend on the extraordinary attraction of this substance for moisture. Before, however, fully following out the clew thus obtained, we made a similar study of the iodide of antimony.

The iodide of antimony was prepared like the bromide, by shaking up in a glass flask a solution of iodine in bisulphide of carbon with finely pulverized metallic antimony. On filtering and decanting, after the color of the iodine is discharged, a solution having a pale greenish-yellow color is obtained, from which on cooling or on evaporation red crystals of iodide of antimony are deposited. The substance may be purified by recrystallization from the same solvent; but iodide of antimony is far less soluble in bisulphide of carbon than the chloride or bromide, and cannot therefore be so advantageously treated in this

way, nor can the small amount of carbonaceous impurity which the crystals acquire from the solvent be so easily removed. Moreover, iodide of antimony cannot be so readily distilled as the chloride or bromide, on account of its high boiling point, which is above that of metallic mercury. But another property of iodide of antimony which, so far as we know, has not hitherto been noticed, interferes still more seriously with these methods of purifying this substance. In all its conditions, it undergoes a more or less rapid oxidation in contact with atmospheric air, forming oxi-iodide of antimony (SbOI) and free iodine. When iodide of antimony is rapidly boiled in a small flask, so that the body and most of the neck are kept full of vapor at the boiling-point, the action at the surface of contact of the vapor and the air is very striking; iodine is set free in vapor, with its familiar violet color, while the oxi-iodide is precipitated in clouds, forming a most beautiful phenomenon. So also when the greenish-yellow solution (above described) of the iodide in bisulphide of carbon is exposed to the air and light, it rapidly becomes colored red from the liberation of iodine, and at the same time turbid from the deposition of the insoluble oxi-iodide. Even the crystals of iodide of antimony, when kept in the light, slowly become opaque from the formation of the same oxi-iodide; while the odor and staining of the stopper of the bottle furnish abundant proof of the liberation of iodine. The study of these phenomena was most interesting, and the results obtained will be described in another paper. It is sufficient for the present to say that they pointed out to us a great source of impurity in iodide of antimony, and fully explained the want of accordance in our analyses of the crystals of this substance as first prepared. It was evident that we could only hope to purify the material by distilling or subliming it in an atmosphere of inert gas; and we devised the apparatus represented in the accompanying figure for this purpose, which we have since found very generally useful for all sublimations where the temperature required does not exceed that which can be measured with a mercury thermometer. The apparatus has been already referred to (page 26), and requires no further description. It was a simple modification of the apparatus used before for drying at a regulated temperature the precipitates of sulphide of antimony, which, as we have stated, was so arranged that the character of any sublimates which might be given off could be observed. We used the same glass tube passing through the sheet-iron air-bath, with its transparent mica cover, only we added a common glass adapter, selected so that its mouth just fitted over the open end of the tube. A platinum nacelle containing iodide of antimony, which had

already been purified by crystallization, was placed in the tube within the air-bath, but near the open mouth; and, while a current of dry carbonic dioxide through the apparatus was steadily maintained, the air-bath was heated by a gas lamp to the required temperature which was



indicated by a thermometer, as shown in our figure. Iodide of antimony is sensibly volatile, even at 100°; and long before it reaches its melting point, 167°, the evaporation becomes very marked. As soon as melted, it sublimes quite rapidly; and we obtained the best results by keeping the temperature between 180° and 200°, and, by shifting the adapters we used as receivers, it was easy to collect the different portions of the sublimate. We thus obtained crystals of two isomeric modifications of iodide of antimony: the more abundant in large hexagonal plates, often half an inch or more in diameter, perfectly transparent, and of the most brilliant ruby-red color; the other in small rhombic plates, having the same peculiar greenish-yellow color as the solution of the iodide already mentioned. The amount of the last was always small, but it was larger in proportion as the temperature was lower. This new and most interesting product will be described in the paper just referred to. Of these crystals, the most brilliant, chiefly of the red variety, were selected for analysis. The iodine determinations were conducted in all respects like those of chlorine and bromine. The iodide was first dissolved by a very concentrated solution of tartaric acid, and then the solution was diluted to the required extent. The same care was taken not to add more than a very slight excess of argentic nitrate, and the amount required was accurately weighed out in each case. Each of the determinations was made with a separate preparation in so far as it was a product of a separate sublimation; but the material sublimed was essentially the same in all cases, — a mixture of the products of many crystallizations from the crude material made as described above. The results are collected in the following table: —

Analysis of Iodide of Antimony.

Iodine Determinations.

No.	Wt. of SbI_3, grammes.	Wt. of AgI, grammes.	% of Iodine, I = 127, Ag = 108.	Variety.
1.	1.1877	1.6727	76.110	Pure red.
2.	0.4610	0.6497	76.161	Chiefly yellow.
3.	3.2527	4.5716	75.956	Pure red.
4.	1.8068	2.5389	75.939	Pure red.
5.	1.5970	2.2456	75.990	Red and yellow.
6.	2.3201	3.2645	76.040	Pure red.
7.	0.3496	0.4927	76.161	Chiefly yellow.

Mean value	76.051
Theory Sb = 120, requires . .	76.047
Theory Sb = 122, „ . .	75.744

If in calculating the results of these iodine determinations we use the atomic weights of Stas, I = 126.85 and Ag = 107.93, the mean value would be 76.034, and the corresponding atomic weight of antimony 119.95.

The difference (0.004) between the first mean value and theory — corresponding to only about $\frac{2}{10}$ of a milligramme in the largest amount of argentic iodide weighed — is evidently insignificant, so that these results confirm the lower value of the atomic weight of antimony as closely as did the analyses of the bromide.*

* After the success we had in the application of our method of sublimation to purifying the iodide, we attempted to purify the bromide of antimony in the same way. We thus obtained a very beautiful product, free from every trace of impurity except hygroscopic moisture. The last could not be avoided without more efficient means than we then had of drying the necessarily somewhat rapid gas current; but we were satisfied that with proper precautions, this would be a better method of preparing pure antimonious bromide than the one

As we have already intimated, our analyses of the iodide of antimony, as first crystallized from bisulphide of carbon, yielded very discordant results. These we give in the table below, not, as before, in the exact order in which the analyses were made, but in the order of the several values, so as to exhibit the distribution of the errors.

ANALYSES OF CRYSTALLIZED ANTIMONIOUS IODIDE, RED VARIETY.

No.	% of Iodine.
1.	75.71
2.	75.76
3.	75.78
4.	75.80
5.	75.84
6.	75.85
7.	75.87
8.	75.89
9.	75.94
Mean value	75.83
Theory Sb = 122	75.74
Theory Sb = 120	76.05

The cause of this discordance we attributed, as we have intimated, chiefly to the remarkable readiness with which iodide of antimony undergoes oxidation in contact with the air, resulting in the formation of oxi-iodide of antimony and free iodine, thus:—

$$2\,SbI_3 + O\text{-}O = 2\,SbOI + 2\,I\text{-}I.$$

While the free iodine escapes, the oxi-iodide remains as an impurity in the preparation, and the effect is a replacement of a portion of its iodine by oxygen. Now, since eight parts of oxygen replace one hundred and twenty-seven parts of iodine, it can readily be seen that an otherwise almost imperceptible amount of oxidation would be sufficient

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we employed. For the reasons stated the results of the analyses of the preparations we made in this way were not as concordant as those exhibited on page 54, although the close agreement of the mean result with that above given was very striking, and in one analysis, using three and one-half grammes of carefully selected material, we obtained 66.662% Bromine.

to produce all the variation from the normal composition which the above results present. A simple calculation will show that an absorption of only $\frac{47}{1000}$ths of one per cent of oxygen, or less than half a milligramme by each gramme of iodide of antimony, would reduce the per cent of iodine from the theoretical value, 76.047, to the mean of the above results, 75.832; and that a corresponding absorption of three-quarters of a milligramme would reduce the per cent to 75.700, the lowest observed. It is not, therefore, surprising that we could obtain concordant results only with material which had been both purified by crystallization and also *recently* sublimed.

Returning now to discuss again the cause of the disagreement of the analyses of antimonious chloride with our otherwise consistent results in regard to the atomic weight of antimony, it was obvious that the strong hygroscopic power of the chloride must lead to a replacement precisely similar to that which is produced in the iodide by direct oxidation; for, as we have before said, the crystals of antimonious chloride cannot be exposed to the atmosphere for an instant without absorbing a perceptible amount of moisture, and every molecule of water thus absorbed reacts on a molecule of the chloride, thus: —

$$SbCl_3 + H_2O = SbOCl + 2\,HCl.$$

And when the antimonious chloride is boiled, the hydrochloric acid formed is given off, while the oxichloride remains behind, dissolved in the great mass of the liquid. Indeed, it seems impossible, with our ordinary appliances, to prepare or purify antimonious chloride without its becoming contaminated with oxichloride; and our experiments would indicate that when once it has been formed, as above described, in the mass of the material, it cannot be wholly removed by distillation or crystallization, however often these processes may be repeated.

Naturally, our attention was very early called to this obvious source of impurity in the antimonious chloride we prepared; and we noticed from the first that, even after the material had been many times distilled, there was always left, on repeating the process, a very small amount of dark-colored residue. We had examined the residue, and found that it was a mixture of chloride and oxichloride of antimony, colored by a trace of carbonaceous material; and we had made a long series of analyses for the purpose of studying the effect produced by the action we have described. The result of these analyses is given in the following table. We started with material already purified by fractional distillation and crystallization, and distilled it ten times in succession; not, however, carrying the distillation to absolute dryness, but leaving, so

far as we could judge by the eye, about the same amount of residue in the retort each time. These residues we analyzed, as we did also the final distillate. The material first distilled was the same as that marked *c* in the table on page 40, and we assumed that the average of the results there given truly represented its composition.

Analyses of Antimonious Chloride.

Residues and Distillates.

	% of Chlorine.
The original purified preparation	46.64
The residue of 1st distillate	45.71
" 2d "	45.66
" 3d "	46.03
" 4th "	46.26
" 5th "	46.26
" 6th "	46.00
" 7th "	46.03
" 8th "	45.94
" 9th "	45.65
" 10th "	45.99
The last distillate	46.62

Although, under the circumstances, we could not expect great precision, yet it was evident from these analyses that the amount of impurity in the residues was not diminished by the successive distillations; and we therefore concluded that additional oxichloride of antimony must be formed each time during the very short contact with the atmosphere which the transfers between the several distillations necessarily involved. But, on the other hand, the very remarkable fact that these ten distillations produced no sensible change in the composition of the great mass of the material seemed to indicate equally clearly that this action of the atmosphere had no perceptible influence on the final result; and this opinion was still further strengthened when, on twice distilling portions of the last distillate, at a low temperature, in a current of dry hydrogen, we obtained products giving again — very nearly at least — the same per cent of chlorine. And, lastly, when to all this evidence were added the results of the complete analysis of the chloride, showing an amount of antimony which fully supplemented

the very constant per cent of chlorine, the assumption that any material amount of impurity could be present appeared wholly untenable. Yet we have seen how this assumption was forced back upon us by the subsequent results of the investigation.

Returning to the subject after our experiments with iodide of antimony, we, for the first time, fully appreciated how very small an amount of oxygen — the only real impurity present — was required to reduce the per cent of chlorine in antimonious chloride from 47.02, the amount corresponding to $Sb = 120$, to 46.61, which corresponds to $Sb = 122$; for, while the effect is so differently produced, yet the result of the action of the atmosphere on the chloride of antimony is wholly like that of its action on the iodide. It ends in replacing a small amount of chlorine by oxygen; and although, in consequence of the smaller atomic weight of chlorine, it requires in this last case a larger replacement to produce a corresponding change of percentage composition, yet still the amount required to make all the difference in question is very small; so that, when we come to sum up the supposed completed results (as on page 42), it might easily be covered up by slight inaccuracies of the analytical work. An easy calculation will show that the substitution of but $\frac{146}{1000}$ of one per cent of oxygen for the equivalent amount of chlorine would reduce the per cent of this last element in the chloride from 47.020, corresponding to $Sb = 120$, to 46.608, which corresponds to $Sb = 122$; and such a substitution would result from the absorption of only $1\frac{6}{10}$ milligrammes of water by each gramme of the chloride. The composition of the material would then be as follows: —

Composition of Antimonious Chloride with $\frac{146}{1000}$ % of O when $Cl = 35.5$ and $Sb = 120$.

Chlorine	46.608
Oxygen	.146
Antimony	53.246
	100.000

Now it will be seen by referring to the tables, on pages 40 and 42, that these percentages do not differ from the mean of the results of our previous analyses as much as these results differ among themselves; and we therefore determined to repeat these analyses, hoping that the experience we had acquired in both chlorine and antimony determinations would now enable us to obtain results sufficiently sharp to show even

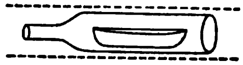
the small differences of composition which the substitution in question would produce.

Meanwhile, we instituted a series of experiments with a view of studying the decomposition which the oxichloride of antimony undergoes under the action of heat, in the hope that we might thus discover some method by which the amount of oxichloride of antimony in our preparations might be directly determined. For this purpose, we used first crystallized SbOCl, obtained by the action of alcohol on chloride of antimony in a sealed tube, which we weighed out into a platinum nacelle, and heated to various regulated temperatures, using for this purpose the apparatus already described. It appeared that the decomposition took place in two stages. The first stage of the decomposition began between 167° and 175°, but was not completed until between 260° and 280°. The second stage began at about 320°, but required for its completion a red heat. During both stages, chloride of antimony sublimed; and there was left in the nacelle at the close of the process beautiful crystals of Sb_2O_3. In another experiment, we used crystallized $Sb_4O_5Cl_2$, prepared in the same way as the SbOCl, but with different proportions of alcohol and chloride of antimony. In this case, the decomposition did not begin until 320°, but in other respects both the process and the products were as in the first experiment. It was quite evident that the chemical changes which took place in the two stages of decomposition we have noticed were represented by the following reactions: —

First stage: $$5\ SbOCl = Sb_4O_5Cl_2 + SbCl_3; \qquad (1)$$

Second stage: $$3\ Sb_4O_5Cl_2 = 5\ Sb_2O_3 + 2\ SbCl_3; \qquad (2)$$

but the relative weights observed in the first two experiments were of no value, because it was evident that a no inconsiderable amount of Sb_2O_3 was lost by sublimation. Since, however, the small sublimate of oxide condensed in the glass combustion-tube very much nearer the nacelle than the very much larger sublimate of chloride, we varied the apparatus in our third experiment so far as to place the nacelle in a tube of the shape represented in the accompanying figure. This tube was weighed with the nacelle, and was so selected that it quite closely fitted the combustion-tube within which it was placed for heating, as shown in figure by dotted lines. And it is evident that, while with this arrangement the $SbCl_3$ would be swept



by the CO_2 gas into the colder portion of the combustion-tube, the greater part at least of the sublimed oxide would be retained in the small tube, which was of course at each stage weighed with the nacelle as at first. Our results were as follows: —

Weight of SbOCl	0.4939	grammes.
Loss at 280°	0.1271	"
Required by theory of reaction 1, if Sb = 120	0.1305	"
Total loss at red heat; that is, in both stages .	0.2179	"
Required by theory of reactions 1 and 2 . .	0.2174	"

It was evident from this determination that the order of the decomposition was precisely that indicated by our reactions, although the end of the first stage was not quite so sharply marked as the end of the second; and this would naturally be expected.

As the residues obtained on distilling chloride of antimony showed, when further heated, precisely the same order of phenomena which we have just described, and when heated to redness yielded the same crystals of oxide of antimony as before, it was plain that the residue left on evaporating the chloride at a temperature not exceeding 120° was chiefly at least SbOCl; but that this when heated more intensely was converted into $Sb_4O_5Cl_2$ before the temperature reached 280°, and finally at a red heat was converted wholly into Sb_2O_3. We therefore endeavored to determine the amount of oxichloride in one of our preparations of chloride of antimony by distilling a weighed amount from a platinum nacelle at as low a temperature as possible in a current of dry carbonic acid, and heating the residue to a temperature of about 275°. We thus obtained the following results: —

No.	Wt. of $SbCl_3$.	Residue.	% of Residue $Sb_4O_5Cl_2$.
1.	6.7286	0.0212	0.315
2.	4.5150	0.0151	0.334
3.	7.9320	0.0258	0.325

In order to yield 0.146 % of oxygen, which would reduce the per cent of chlorine in the preparation from 47.020 to 46.608, as in the scheme on page 62, there would be required 1.155 % of $Sb_4O_5Cl_2$.

Although the results of the above determinations accord within a few per cent of the quantity estimated, yet it was perfectly clear dur-

ing the course of the experiments that they did not at all represent the total quantity of the oxichloride present in the preparation examined. Not only was the composition of the preparation not materially altered by the slow distillation, — a fact shown by the determinations marked *e* in the table on page 40, and by which we were misled at the outset, — but also the product from our distillation yielded when distilled again apparently as much residue as before. In a word, we found the same phenomena repeated in these distillations at a low temperature which had been so noticeable when the chloride was distilled at its boiling point, and which are so strikingly illustrated by the results given on page 61. It is possible, as before suggested, that the effects might arise from a small additional absorption of water at the successive transfers which the repeated distillations involved; or, in the later experiments, from the circumstance that the very extensive apparatus employed for drying the carbonic dioxide was not completely effectual. Still, now that our attention had been called to the danger, and we had taken unusual precautions on both these points, the explanations suggested did not seem to us sufficient; and we came to the conclusion that the oxichloride must distil over with the chloride of antimony to a certain limited extent, and that it was only an excess above this definite amount which was left behind as residue. Of course, SbOCl not only is not volatile, but is at once decomposed by heat; and we do not suppose that this compound by the tension of its own vapor is carried over in distillation. It is a very dilute solution, as it were, of SbOCl in $SbCl_3$ which thus distils; and the distillation of the oxichloride may resemble the carrying over of boracic acid by the vapor of water, and similar phenomena, the result, as it is has always appeared to us, of a feeble kind of chemical union which has been usually designated by the term "molecular combination." Such a theory would account for the remarkable constancy which we have found in the chlorine determinations of the various preparations of antimonious chloride purified by distillation. But, on account of the very great difficulty of removing all possible disturbing causes, we found it impossible to obtain a rigid experimental demonstration of our theory without much more time and labor than we could then command. We hope to return to the subject hereafter. Meanwhile, however, it was evident that we could place no reliance whatever on the results just obtained. Nevertheless, the determinations were of value on account of the contrast between these results and those of a similar series of experiments on the residues from antimonious bromide which we collect in the following table: —

No.	Wt. of $SbBr_3$.	Residue chiefly $Sb_4O_5Br_2$.	% of residue.
1.	2.8342	0.0010	0.035
2.	2.0220	0.0006	0.030
3.	4.6730	0.0010	0.021

As will be seen, this residue is less than one-tenth of that obtained from the chloride, and is practically insignificant. Evidently, then, in the determination of the atomic weight of antimony more accurate results may be expected from the analysis of the bromide than from the analysis of either the chloride or the iodide of this element. The intermediate position of the bromide renders it, in a very remarkable way, the most stable of the three compounds. It absorbs moisture far less eagerly than the chloride, and it absorbs oxygen far less readily than the iodide, and is thus in great measure protected against each of these two sources of the same impurity.

We come finally to the new analyses of antimonious chloride we had undertaken. Fortunately, some of the old preparation that had been distilled so often had been preserved. It had been boiled for a long time since the last analyses were made, and kept in the same flask used for determining its boiling point, which had stood meanwhile tightly corked in a desiccator over sulphuric acid. The solid mass in the flask was easily broken up without exposure to the air by simply heating it to the melting point, and shaking it in the flask as soon as, beginning to melt, the mass had separated from the glass. Near its melting point, chloride of antimony becomes very friable, and is thus easily reduced to coarse powder, whence probably the old alchemistic name of butter of antimony. It is also worthy of notice that neither the bromide nor the iodide acts in this way, as we found out in more than one instance to our cost.

Thus we were readily able to prepare our material for analysis, and, by a thorough mixing of the mass, to insure that the several samples taken had a uniform composition. In regard to the antimony determination, no further details are necessary. It was conducted, as described before, with every minute precaution which experience had suggested; and we give the full details, in order to show how completely we had been able to overcome the difficulties which it at first presented, and we feel confident that there is no process of wet analysis which is capable of giving more accurate results than this.

Details of Antimony Determination.

The antimonious chloride was first transferred to a very carefully dried weighing tube, and thence to the large flask in which it was dissolved. The transfer to the weighing tube was made in a dry atmosphere, and only required two or three seconds. It is evident, however, that a slight absorption of moisture at this point is not important; for, even if it increased the apparent weight of the assay by several milligrammes, it would only reduce to a barely perceptible extent the percentages of all the constituents leaving the relative values wholly unchanged. It is only when, on boiling the chloride, after such an absorption, the chlorine is driven off, that the essential change of composition results.

Weight of tube and antimonious chloride .	20.9609	grammes.
„ „ after transfer to flask . .	16.3920	„
„ chloride analyzed	4.5689	„

The weight of the tube and chloride while on the balance pan remained invariable for a sufficient length of time to give positive assurance of the constancy of the weights. The chloride was dissolved in a saturated solution of tartaric acid containing about 15 grammes of the pure acid, and then diluted with carbonic acid water and precipitated as before described. The precipitate, having been washed and collected as before, was dried in an air bath, at about 110°.

Weight of small filter	0.0434	grammes.
„ porcelain crucible	101.2132	„
	101.2566	„
„ crucible and precipitate . .	104.6762	„
„ red sulphide of antimony .	3.4196	„

A portion of the dried precipitate dissolved in hydrochloric acid gave no residue. The rest was then transferred to a platinum nacelle, and heated, as has been described, in a current of dry carbonic dioxide

gas. No sublimate was formed, and only a very slight empyreumatic odor could be perceived.

Weight of platinum nacelle	6.2493	grammes.
„ nacelle and dried precipitate . . .	9.5273	„
„ portion taken	3.2780	„
„ nacelle and precipitate after heating to 285° for over half an hour .	9.5234	„
Loss of weight of portion taken	0.0039	grammes.
Corresponding loss for whole precipitate . .	0.0041	„
Weight of red sulphide as above	3.4196	„
„ gray sulphide	3.4155	

The carbonaceous residue left on dissolving this whole amount of gray sulphide in hydrochloric acid was barely perceptible. It was collected, however, as usual, on a weighed paper disk, and estimated.

Weight of small paper filter	0.0198	grammes.
„ same with residue	0.0212	„
„ residue	0.0014	„
Calculated for whole precipitate	0.0015	„
Weight of gray sulphide as above	3.4155	„
Total weight of gray sulphide	3.4140	„
Corresponding weight of antimony assumed to be $\frac{5}{7}$ of the sulphide	2.4386	„
Per cent of antimony in the antimonious chloride under examination	53.374	„

It will be noticed that this result is practically identical with the mean of the previous determinations, which, as will be seen by reference to the table on page 42, was 53.401; and, by reviewing the facts stated in that connection, it will be perceived that this agreement is in itself alone a strong confirmation of the conclusion which we deduced from our first experiments on the synthesis of the gray sulphide of antimony, — that of the two values of the atomic weight of antimony in question, the lower is the more exact.

Coming next to the chlorine determinations, we noticed, for the first time, an effect which, under certain circumstances, may have an important influence on the accuracy of this well-known process, as employed in the analysis of chloride of antimony. In a precipitate of argentic chloride that had been deposited from an unusually concentrated solution of antimonious chloride in tartaric acid, and had stood over night, our attention was called to some crystalline grains, which, on examination, proved to be a compound of tartaric acid, antimony, and silver. We soon found that this product could be readily obtained by concentrating the filtrate from the precipitate of argentic chloride, and adding to it, while still warm, an excess of argentic nitrate. On cooling, the new crystals form in abundance. They have not yet been measured, but under the microscope they have the general aspect of right rhombic plates or prisms, with hemihedral modifications, — a general form which is so characteristic of the tartrates, and which we ourselves have previously studied in our crystallographic determinations of the tartrates of rabidium and cæsium.* We obtained for the amount of silver in the crystals, as a mean of three analyses, 26.30 per cent. The compound $Ag,SbO,H_2\equiv O_4\equiv(C_4H_2O_2) . H_2O$ would require 26.34 %. The crystals may therefore be regarded as tartar emetic, in which the potassium has been replaced by silver; and they resemble the crystals of this well-known salt in general form. They are evidently the same substance obtained by Wallquist† by precipitating nitrate of silver with tartar emetic, and analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27.31 and 28.05 per cent of oxide of silver, which corresponds with the result given above as closely as could be expected; but they appear to have prepared the substance only in an amorphous condition. At least, in the description quoted, no mention is made of any crystalline form.

These crystals of argento-antimonious tartrate are apparently not acted upon in the least by cold water, and only slightly by boiling water; and finding this very insoluble material mixed with the precipitated chloride of silver, under the conditions stated, we were led to fear that it might be occluded to some extent by this precipitate, even when formed in much more dilute solutions of antimony and tartaric acid. The phenomenon was very similar to that we had already studied in the occlusion of the oxichloride by the sulphide of antimony; and there was reason to fear that, as in the previous case, an occlusion of this

* Am. Jour. of Science and Arts. (2), xxxvii. 70.

† Gmelin Handbook, Cavendish Edition, x. 826.

double tartrate might result, even when the substance would not otherwise be precipitated. How far such an action could have vitiated our previous results, it was, of course, now impossible to determine; but, as we previously stated, we had always taken great care not to add more than the slightest possible excess of argentic nitrate, and this was especially true in our more recent determinations. Now, however, we were on our guard, and in the following determinations very great pains were taken to add just the requisite amount of the silver salt, and the argentic chloride was subsequently examined for traces of any such occlusion. But, excepting this close attention to well-known precautions, the determinations were made in the same way as before.

ANALYSIS OF ANTIMONIOUS CHLORIDE.

No.	Wt. of $SbCl_3$.	Wt. of AgCl.	% of Chlorine.
1.	2.2220	4.1682	46.407
2.	1.9458	3.6512	46.420
Mean value	. . . .		46.413

Bringing now the results together, — estimating the amount of oxygen by difference, as is usual in chemical analysis, and calculating what would be the composition of a preparation of antimonious chloride in which $\frac{213}{1000}$ of a per cent of oxygen had replaced an equivalent amount of chlorine, assuming, of course, Sb = 120 and Cl = 35.5, — we obtain the following very striking accordance: —

	Analysis.	Theory. Sb = 120, Cl = 35.5.
Chlorine	46.413	46.418
Oxygen	.213	.213
Antimony	53.374	53.369
	100.000	100.000

The general conclusions, then, which we deduce as the results of this investigation, are —

First, that the value of the atomic weight of antimony found by Schneider in 1856 — Sb = 120.3 — must be accurate within a few tenths of a unit, but that the most probable value of this constant, as deduced from our experiments, is Sb = 120, when S = 32.

Secondly, that the apparent disagreement with this result, presented by the partial analyses of antimonious chloride, is *probably* due

to the constant presence of oxichloride in the preparations of this compound.

The investigation from the first has been a study of constant errors; and those who have followed us through the details will certainly allow that the opinions expressed at the beginning of this paper (on page 9) were not hastily conceived, even if they do not fully agree with our conclusions. In the attempts to correct or balance such errors, we have found at once the chief difficulties and interest of our work, and the secondary results thus reached seem to us the most important fruit of the whole investigation. Seeing, then, the sources of constant error we have discovered, and knowing that there are others whose influence we have been able to trace, although we have not been able to define them as clearly as we could desire, it would be presumptuous in us to express too great confidence either in the correctness of our theories or even in the conclusiveness of our experimental results. Of this, however, we feel assured, that more trustworthy results cannot be expected from a repetition of the same processes until a more complete and accurate knowledge has been acquired of the substances employed. We have therefore proposed to ourselves a more thorough investigation of the haloid compounds of antimony, and the first results of this investigation we shall shortly publish. After the requisite data have been thus collected, we hope to return to the old problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.

During the course of this investigation, we have been successively aided in the experimental work by Dr. F. A. Gooch, Mr. C. Richardson, and Mr. W. H. Melville, at the time students in this laboratory; and without their assistance we could not have accomplished the great amount of labor it involved.

HARVARD COLLEGE LABORATORY, *June 12th*, 1877.

II.

RE-EXAMINATION OF SOME OF THE HALOID COMPOUNDS OF ANTIMONY.

By Josiah P. Cooke, Jr.,

Erving Professor of Chemistry and Mineralogy in Harvard College.

Our chief object in this paper is to describe some remarkable crystallographic and chemical relations of antimonious iodide, first noticed during the investigation of which an account has just been given; but we will also take the opportunity to give the results of some observations upon antimonious chloride and antimonious bromide, as well as upon the oxichlorides, oxibromides, and oxi-iodides of antimony, all of which have more or less bearing on the principal subject.

Antimonious Chloride ($SbCl_3$).

Very perfect and brilliant crystals of antimonious chloride can be made in one of two ways, and both methods yield crystals of the same general form and habit.

The first method consists in cooling a saturated solution of the chloride in carbonic disulphide. Antimonious chloride is very soluble in this liquid, when near its boiling point; but the solubility diminishes very rapidly with a falling temperature, and, when the solution is cooled with a freezing mixture, by far the larger part of the substance crystallizes out. During our experiments, we frequently noticed, with these solutions of antimonious chloride, the phenomena of supersaturation. A solution saturated at the boiling point of the solvent, and cooled in a clean glass flask, may, if undisturbed, remain liquid for an indefinite time; but, the moment a bit of the solid substance is dropped in, the crystals form with great rapidity, and the very marked rise of temperature which we have observed under these circumstances indicates that the crystallization is attended with the liberation of an unusually large amount of latent heat. Similar phenomena of supersaturation we noticed with solutions of antimonious bromide, which, although less soluble than the chloride, dissolves very freely in the same solvent;

but, with the solutions of the far less soluble antimonious iodide (in disulphide of carbon) the phenomena were not perceptible. It is evident, from these facts, that the phenomena of supersaturation are not confined to aqueous solutions, or to substances which take into their crystalline structure a portion of the solvent, like water of crystallization.

The second method of obtaining crystals of antimonious chloride, is the familiar process of pouring off the still fluid portion, after the melted substance has partially solidified. Since, in consequence of the low temperature at which it hardens and the large amount of latent heat evolved in the process, the chloride *sets* comparatively slowly, the crystals form under these circumstances with great perfection, and are left clear and brilliant when the fluid is poured off.

It is very easy to obtain, by either of these methods, very perfect crystals, with very brilliant faces; but to measure these crystals is a difficult problem, which we have as yet been able to solve only imperfectly. Antimonious chloride is so very hygroscopic, that, during the short time required to isolate the crystals and mount them in tightly corked glass-tubes (and under such protection the measurements were made), the faces so far lost their lustre as to render the reflected image of the goniometer signal indefinite. Hence, the results given below are to be regarded as only approximate, and may be in error to the extent of even a degree. The angles of the vertical prism are probably the most accurate, because the crystals could be most quickly mounted with this dome parallel to the axis of the tube. The two domes present were measured on different crystals, and the angles given are the results of what were considered the most favorable observations. When the crystal was once mounted, its position could not be shifted; for the antimonious chloride attacked the wax used, and this circumstance added to the difficulties attending the necessary manipulations in measurements with the goniometer.

The crystals of antimonious chloride are trimetric, and have the same general habit whether obtained by the one or the other of the two methods just described. The chief difference is a greater or less degree of elongation in the direction selected as the vertical axis, — a difference which is shown by Figs. 1 and 2 of Plate I. The crystals were examined with a polarizing microscope arranged as a stauroscope; and we observed that, when the crystals were resting on either of their planes, so that the light passed between two opposite and parallel surfaces, the principal optical sections were, as nearly as could be observed, either parallel or normal to the prismatic edges. This, although not

conclusive evidence in itself, confirms the conclusion in regard to the crystalline system, which was based on the symmetry of the external form.

Crystalline Form of Antimonious Chloride.

Orthorhombic System.*

Forms {110} and {011}

Figs. 1 and 2, Plate I.

$a = 1.263 \quad b = 1 \quad c = 1.109$

Angles between normals.

110 on $1\bar{1}0 = 103° \ 16'$

011 „ $0\bar{1}1 = 115° \ 57'$

In order to obtain the specific gravity of antimonious chloride in the solid state, we filled a specific-gravity bottle nearly full of the melted substance; and, after the mass had "set," we added (so as to completely fill the bottle) some rock oil, which had been rectified over sodium. We then kept the bottle in the exhausted receiver of an air-pump, long enough to remove any entangled air; and, finally, after inserting the ground stopper and wiping away the excess of oil, we took the weight at a carefully regulated temperature. We could find no liquid on which antimonious chloride does not act, to a greater or less extent. It acted slightly even on this rectified rock oil, although only very slowly; so that, by working as quickly as possible, we must have obtained a result which was at least nearly accurate. We used the same preparation of antimonious chloride, of which a complete analysis is given on page 70 of the previous paper. The weight taken was 19.9575 grammes, which displaced 5.0212 grammes of oil. The specific gravity of the rock oil at 26°, referred to water at the same temperature, was 0.7693; and we found —

Specific gravity of Antimonious Chloride at 26°, referred to rock oil at same temperature . .	3.976
Specific gravity of Antimonious Chloride at 26°, referred to water at same temperature. . .	3.064

The melting point of antimonious chloride was determined by observing the constant temperature during the slow crystallizing of a considerable mass of the melted substance, the liquid being stirred

meanwhile with the bulb of the thermometer, which was immersed up to the division on the stem marking 15°. The preparation used in this determination was that designated by *f*, in the table on page 40; and we obtained, as the

Melting point of Antimonious Chloride, 72° C.

We obtained also, and in the usual way, for the

Boiling point of Antimonious Chloride, 216° C.

In several instances, while rectifying this substance as described in the last paper, we followed the boiling point, and observed that it was constant, during the whole period of the distillation.

Antimonious Bromide ($SbBr_3$).

The methods used for preparing and purifying the bromide, as well as the chloride, of antimony, have been so fully described in the previous paper that no further details are necessary here. We obtained very brilliant crystals of the bromide, not only by the two methods described under the last head, but also by sublimation with the apparatus represented on page 57 of this volume. As treated in either of these ways, the habit of the substance is to form needle-shaped crystals, which run out into fine points without definite terminations, and often group themselves into irregular bundles, — a very common feature of this type of crystals. Only on one occasion (then by slowly cooling a solution in disulphide of carbon) did we obtain well terminated crystals; and, although we afterwards tried again and again, we have not yet been able to reproduce them. Unfortunately, moreover, before we were ready to make our measurements, the small terminal planes of these crystals had already become tarnished by the atmosphere. For, although the substance is so much less hygroscopic than antimonious chloride, yet the crystals of antimonious bromide soon lose their sharpness, if exposed even to what we call our dry winter air. Hence, we were not able to measure the angles between the terminal planes with a reflective goniometer. The approximate value of 101 on 100, we obtained by measuring the corresponding edge angle under the microscope, and by frequent repetitions of the measurement on different crystals, or on the two sides of the same crystal, securing as great accuracy as is possible under such circumstances; but the result cannot be relied upon within one or two degrees.

Crystalline Form of Antimonious Bromide.

Orthorhombic System.

Forms {100}, {010}, {101}, {110}, {111 (?)}

Fig. 3, Plate I.

$a = 1.224 \quad b = 1 \quad c = 1.064.$

Angles between normals.

010 on 110	39° 14′
Also, measured with microscope.	
101 on 100	49° approximately
Calculated.	
101 „ $\bar{1}01$	82°
111 „ $11\bar{1}$	72° 4′
111 „ 010	38° 47′
111 „ $\bar{1}11$	61° 30′

The octahedral angles were calculated on the assumption that the observed planes were those of a fundamental octahedron; but, although the intersections with 110 appeared to be parallel, yet the edges were too indefinite to give any certainty on this point.

We also examined the crystals of antimonious bromide with the polarizing microscope, and observed that one of the principal optical sections was parallel to the prismatic edge, whether the light passed normal to one or the other of the two pinacoids 010 and 100. *

The specific gravity, in the solid state, of purified antimonious bromide was taken in precisely the same way as that of antimonious chloride: —

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* The only previous description of these crystals of which we have any knowledge was given by Nicklès, "Comptes Rendus," XLVIII. 837, in these words: "Le bromure d'antimoine se présente en otaèdres rhomboidaux, parfois modifiés par des faces terminales; ils constituent alors des prismes aplatis de 69 degrés terminés par des pointements de 80 degrés; l'angle de deux faces contigués de l'octaèdre est de 181 degrés (les minutes ont dû être negligées le cristal étant trop déliquescent)." In a later paper, "Journal de Pharmacie et de Chimie" (3), XLI. 142, a figure is given, and this description is essentially repeated, correcting the obvious misprint, 181 for 131; but, nevertheless, this error has been very generally copied. The crystals measured by Nickles must have had a very different habit from any we have seen, and we have not been able to reconcile his description with our own observations.

Weight of Antimonious Bromide taken	. .	32.2938 grammes.
Specific gravity referred to Kerosene at 23°	.	5.386
„ „ Water at 23°	.	4.148

By the same methods used with antimonious chloride, we made several determinations of both the melting and the boiling points of purified antimonious bromide, with the following results:—

Melting point of Antimonious Bromide	.	93° C.
Boiling point „ „	.	280° C.

ANTIMONIOUS IODIDE (SbI_3).

There are three crystalline conditions of antimonious iodide, — the hexagonal, the orthorhombic, and the clinorhombic or monoclinic, of which only the first has hitherto been described.

HEXAGONAL ANTIMONIOUS IODIDE.

Hexagonal crystals of iodide of antimony of a deep ruby red color can be readily obtained, either by cooling or by evaporating a saturated solution of this substance in disulphide of carbon, and this solution is easily prepared (as described in the previous paper) by shaking up, with finely pulverized metallic antimony until the color is discharged, a strong solution of iodine in the same solvent. These crystals were described by Nicklès, in connection with those of antimonious bromide, in the paper just referred to. He states that they are hexagonal, double pyramids, with a basal angle of 133°; and his description is referred to by Schneider,* who also obtained hexagonal crystals, both from the disulphide of carbon solution, and also by subliming a mixture of antimonious sulphide with iodine. Schneider speaks of the crystals as brilliant, sharp, six-sided leaves or tables; but gives no additional measurements. All the crystals which we have examined (and we have seen the products of a great number of crystallizations) are combinations of a rhombohedron with its first obtuse rhombohedron and the basal planes, as shown in Figs. 4 and 5, Plate I. The habit of the crystals, however, differs very greatly with the conditions under which they are formed. When deposited during the rapid cooling of a solution saturated at the boiling point of the very volatile solvent, they are, as Schneider states, small and leaf-like, with a very definite hexagonal outline; but still, when seen with a microscope by

* Poggendorff, Annalen, cix. 610, 1860.

reflected light, the rhombohedral planes can be distinguished on the edges. When formed during the slow evaporation of the solvent, they are, as Schneider also noticed, larger and more tabular. We ourselves have further observed, that, when the solution contains an excess of iodine, the rhombohedral planes become much more dominant, and the crystals greatly elongated in the direction of the vertical axis. The basal plane is then often reduced to a small triangular face; and we have seen crystals in which it had almost, if not wholly, disappeared. Among such crystals, we have observed macles hemitroped on the basal section; and the rhombohedral planes are frequently strongly striated parallel to the basal edges.

Under circumstances similar to those just mentioned, especially when the amount of free iodine in the solution is proportionally large, the crystals frequently group together into stars with six rays. These rays are formed by crystals elongated in the direction of one of the diagonals of the hexagonal section, and each by itself has the outward aspect of the trimetric system. The rays often branch, but in all cases at the constant angles of 60° or 120°; and the whole group preserves a more or less regular hexagonal outline. Such groups may be regarded as skeleton crystals, and their formation is probably determined by a deficiency of the substance of the crystals in the mixed solution from which they are formed. The polariscope shows that they have throughout an hexagonal structure, and their formation indicates a tendency in the crystals of this substance (often manifested in single crystals to a less degree) to excessive development in a single direction, thus imitating a trimetric habit. As we shall hereafter see, this habit is not without its significance.

When iodide of antimony is sublimed as described in the previous paper (page 57), and also by Schneider (*loc. cit.*), it condenses in very broad thin leaves or plates, which hang from the surfaces of attachment by their edges. Even these, however, frequently exhibit on their free edges, not only the hexagonal outline, but also the rhombohedral planes; and the polariscope shows that the surfaces of the leaves are simply widely extended basal planes.

Iodide of antimony is not hygroscopic, and for this reason the crystals present conditions which are more favorable for accurate measurements than the crystals either of the chloride or of the bromide of the same element. Nevertheless, our results were not as constant as the brilliancy of the crystals led us to expect; and we met with variations in the angles which we could not ascribe solely to imperfections of the faces or to other causes of inexactness in the measurements. The

uncertainty thus arising does not, however, amount to more than a few minutes. We give the results obtained with the most perfect crystals we could find, on which we were able to measure all the angles of the principal dome between the two basal planes.

Crystalline Form of Antimonious Iodide.

Hexagonal Variety.

Forms {111}, {100}, {011}

Figs. 4 and 5, Plate I.

Angles measured between normals.

111 on 100	72° 28′
100 „ $0\bar{1}\bar{1}$	49° 22′
$0\bar{1}\bar{1}$ „ $\bar{1}\bar{1}\bar{1}$	58° 8′
	179° 58′

These measurements correspond to the dimensions of a modified rhombohedron in which the axes of Miller's system make with each other the angle of 54° 40′, or the vertical axis of Naumann's system has the value $C = 2.769$. The crystals cleave readily parallel to the basal plane.

Angles between normals.	Calculated.	Measured.
111 on 100	72° 38′	72° 28′
111 „ 110	49° 23′	49° 22′
110 „ $00\bar{1}$	57° 59′	58° 8′
100 „ 010	111° 30′	
110 „ 011	94° 28′	
100 „ 110	55° 45′	

The crystals are optically uniaxial with very strong negative double refraction, and the broad plates obtained by sublimation furnish excellent objects for the polariscope; but such preparations are not durable if exposed to the atmosphere, for a reason which will appear further on. The rings of the interference figure, as seen by common light, are nearly black, but with strong-colored fringes, — red on the inside, and greenish yellow on the outside. This is a natural result of the selective absorption of this highly colored medium; but the effect is, nevertheless, very striking.

Evidently, then, so far as yet appears, the iodide of antimony is not isomorphous with the corresponding bromide and chloride, although there is no group of compounds which we should by analogy expect to find more closely isomorphous than the chloride, bromide, and iodide of the same element. It has been shown, however, by other crystallographers as well as by ourselves, that the hexagonal forms are closely related to the trimetric, and that when the angle of the rhombic prism becomes equal to or even closely approaches 60° or 120°, the last may imitate, if they do not actually assume, both the external aspect and internal structure of the first. We were, therefore, led to suspect that we had before us another example of such a relation, and that the iodide of antimony might thus be constructively isomorphous with its allied compounds. The following calculation, moreover, strongly sustained this view: —

The large development of the pinacoid planes (010 and 0$\bar{1}$0) which is very characteristic of the crystals of bromide of antimony, besides the general form of these crystals (as shown by our figure), indicate very clearly that these pinacoids are the analogues of the basal planes of the hexagonal crystals of iodide of antimony; and, if so, then the isomorphism of the bromide and the chloride indicates that, for the last compound, the analogues of these planes would be a corresponding pair of pinacoids which does not appear on the actual crystals. Again, we find the analogue of the angle, 120°, on the hexagonal section of the crystals of antimonious iodide, in the angle 98°, between the planes 101 and $\bar{1}$01 on the crystals of antimonious bromide; and although the corresponding planes do not appear on the crystals of antimonious chloride, yet the equivalent angle can be easily calculated, and will be found to be 97° 26′. If now we compare the tangents of the halves of these last two angles with $\frac{2}{3}$ of the tangent of 60°, we shall obtain the following relations: —

For $SbCl_3$	tang. 48° 43′	=	1.139
„ $SbBr_3$	tang. 49°	=	1.150
„ SbI_3	$\frac{2}{3}$ tang. 60°	=	1.155

If, further, we take into consideration the third axis, this relation will appear still more close and simple. Making, then, in the crystals of antimonious chloride and bromide the half-axis c our unit, and regarding for the time, as the vertical axis, the half-axis b, which corresponds to the vertical axis of the hexagonal form, giving also to this last axis its known value, — we obtain the following comparison between

the axial dimensions of the two orthorhombic forms and of the hexagonal form, if referred to corresponding orthorhombic system of axes:—

For $SbCl_3$	$a = 1.139$	$\acute{b} = 0.902$	$c = 1$
" $SbBr_3$	$a = 1.150$	$\acute{b} = 0.940$	$c = 1$
" SbI_3	$a = 1.155$	$\frac{1}{3}\acute{b} = 0.923$	$c = 1$

It thus appears that, constructively, iodide of antimony is closely isomorphous with the two allied compounds, and the small apparent differences in the axial dimensions of the three forms are no greater than the uncertainties in these values themselves arising from the imperfect measurements of some of the angles.

But although the rhombic prism of 60° or 120° may imitate the external aspect of an hexagonal form, as is frequently the case with the micas and vermiculites, yet (as the optical relations of these very minerals show) the two classes of forms may still remain perfectly distinct; and it does not, therefore, by any means follow that the rhombic prism passes into the hexagonal system when the prismatic angle becomes 120°. We have, however, shown, in the paper just referred to, that, by a species of interlamination,—interlaminar macling, we may name it,—the orthorhombic crystals of foliated minerals frequently imitate the structure, as well as the forms, of the hexagonal system; and although there is an obvious distinction between such structures and homogeneous crystalline masses, like calcite or the substance we are considering, yet analogy would suggest, that, even the true hexagonal structure may result from a more fundamental macling of the same kind; and we advanced the theory, that it might be the result of what we called molecular macling. According to this theory, the *crystalline* molecules of hexagonal forms are, in some cases if not in all, groups of three simpler molecules, each of which (so far as its chemical constitution is concerned) is a unit in itself, and possibly under certain conditions may act as a unit in a crystalline structure, and probably always becomes isolated when the substance is converted into vapor. Our theory also assumes that the members of these groups are united among themselves in the same relative positions as the diagonals of a regular hexagon, so that the optically uniaxial character of hexagonal crystals is an effect of such grouping, and the hexagonal form an obvious result of the juxtaposition of the six-sided groups. Further, we suppose that the simpler molecules are of such a nature that, when united as individuals in positions parallel to each

other, they would form crystals having a rhombic section of 60° or 120°. The figures 1 and 2, which we reproduce from a previous paper, may help to give a more definite form to these conceptions; but

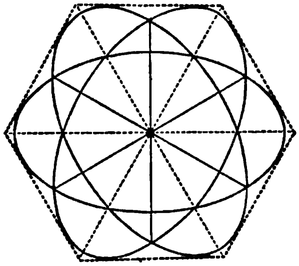


Fig. 1.

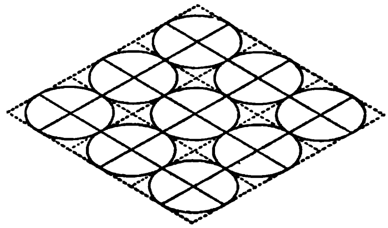


Fig. 2.

such representations are necessarily purely conventional symbols of conditions of which we have as yet no accurate knowledge, and to which, therefore, we can give no definite shape. The capability of such molecular macling as we have described may depend solely on the dimensions of the molecules; and in our figures we have represented such a condition, by giving to the sections of the molecules the form of ellipses of such dimensions that they can be inscribed in the rhomb of 60° and 120°. The conjugate diameters of this figure, when equal, subtend angles of 60° or 120°; and if the poles of the molecules are, as would be natural, at the ends of these lines, then, when the molecules were grouped as shown in Fig. 1, the unlike poles would fall directly over each other; so that the attractive and repulsive forces, centring at the poles, would hold the parts firmly together. The same molecules, if placed parallel to each other (as in Fig. 2), would be also in a stable condition, and the resulting rhombic section would have angles of 60° and 120°. On the other hand, although ellipses of other dimensions might be united as in Fig. 2, so as to give rhombic sections of every possible angle, yet only with ellipses of the dimension we have described, or those closely approaching this condition, would such a grouping be stable as is represented by Fig. 1. Of course, the molecules must have three dimensions; and, as before intimated, the ellipses are only conventional modes of expressing conceptions which are necessarily very incomplete. These symbols, however, will give form to our theory, and show why, among a series of isomorphous compounds crystallizing in the rhombic system, we might expect to find hexagonal crystals wherever among the various molecular

magnitudes the necessary dimensions were realized, although it is probable that there are other conditions which must also concur to produce this result.

Evidently, we have before us just such an isomorphous series as our theory anticipates, — a series of closely allied substances, in which the orthorhombic passes into the true hexagonal structure; and this furnishes us with an excellent opportunity for testing the theory we have advanced. If the crystalline molecules of the hexagonal iodide of antimony are really groups of three of the chemical molecules of this substance, then we might hope to find another condition of this substance in which the molecules were united, as in the crystals of the allied substances presenting rhombic forms with the angles of 60° or 120°; and, if such could be discovered, it would be reasonable to expect differences in the physical properties of the two isomers corresponding to the differences of structure. We were therefore led to search for a rhombic modification of the iodide of antimony, and with what success will soon appear. Before pursuing this subject, however, it will be best to describe some of the other physical properties of the hexagonal iodide.

The color of the hexagonal iodide of antimony is a brilliant vermilion red, which, however, in some preparations, is more or less tinged with yellow, in consequence of oxidation, and the formation of an oxi-iodide on the surfaces of the crystals. The solution of the iodide of antimony in sulphide of carbon has a greenish yellow color, resembling that of uranium glass, and strikingly contrasting with the brilliant red color of the crystals which have been formed from it, — a fact whose significance will hereafter appear.

We made five determinations of the specific gravity of the hexagonal crystals of iodide of antimony; using for the purpose different preparations, and taking the specific gravity under petroleum which had been rectified over sodium, — the only liquid we could find that did not act on the substance. Even the rectified petroleum, however, acted slowly on this, as it did on the allied substances; but, during the time occupied in the determination, the effect was very slight, and no considerable error could have been thus caused. The following are the results of these determinations, all made at a temperature of about 24°C.: —

No.	Weight taken in grammes.	Sp. Gr. at 24°, referred to water at same temp.
1.	6.9730	4.807
2.	10.1393	4.895
3.	5.3506	4.812
4.	7.8868	4.893
5.	2.1517	4.833
Mean value		4.848

We made four observations of the melting point of the hexagonal iodide. For the first, we used a large amount of material, and, by dipping the bulb of the thermometer in the melted mass, observed the constant temperature while it was slowly solidifying. In the other experiments, we melted a few crystals in a glass tube, heated by a bath of sulphuric acid in the usual way. The result in the first determination was 167½°; in the last three, uniformly 167°, which is doubtless the true value. In the experiments with the tube, it was noticed that the point of solidification was about five degrees below the melting point.

Bringing together now the several results, we have the following comparison of the melting points of the three haloid compounds we have studied —

	Melting Point.	Differences.
Rhombic Antimonious Chloride	72°	
		21°
Rhombic Antimonious Bromide	93°	
		74°
Hexagonal Antimonious Iodide	167°	

From this it appears, that, instead of the equal differences we should naturally expect, the difference between the last two values is between three and four times as great as the difference between the first two. According to all analogies, the melting point of the normal iodide of antimony should be 114°; and the greatly higher value which we obtained is still another indication that the hexagonal iodide on which we experimented has an essentially different structure from that of the chloride or bromide of the same element with which it is here compared.

As yet, we have not been able to determine the boiling point of iodide of antimony with any accuracy. It is above, but apparently

only just above, the boiling point of mercury; and, before the observation can be taken, it will be necessary to adapt some form of air thermometer to the necessary conditions.

ORTHORHOMBIC ANTIMONIOUS IODIDE.

We first met with this new substance while examining with a microscope the product obtained by subliming hexagonal iodide of antimony, in the apparatus represented in the accompanying figure, which we described in our previous paper (page 57); and we at once recognized,



both by its color and its form, the isomeric modification of which we were in search. It appeared in small greenish yellow sprays, sparingly distributed among the red plates of the hexagonal iodide. Its color was precisely that of the solution of the iodide in carbonic disulphide; and, as shown in Plate II., the serrated edges of the crystalline sprigs presented very much the appearance of a picket fence, repeating at each point the characteristic angle of 60°.

It soon appeared that the yellow iodide was always formed when iodide of antimony was sublimed at a low temperature, and that this was the one condition necessary. Iodide of antimony begins to volatilize far below its melting point, even at 100° C.; and, if it is sublimed between two watch-glasses at a temperature not exceeding 114°, the yellow modification is the sole product. It condenses them in beautiful feather-like sprays, on which, however, no definite form can be distinguished. The process, also, is exceedingly slow, and the product very small. A much larger yield is obtained when the iodide is sublimed at a temperature just above its melting point, in a current of inert gas sufficiently strong to sweep the vapor at once into a cool condenser, — conditions, which are perfectly realized in the apparatus we have described.

The yellow iodide generally forms but a small portion of the product of the sublimation; but, by carefully regulating the temperature and gas current, the proportion can be largely increased, and it can then be picked out among the scales of red iodide with which alone it is mixed. To obtain, however, in this way, a sufficient quantity of the yellow iodide for analyses wholly free from its more abundant red associate, would have been a very tedious task; but this was not necessary, in order to establish the perfect isomerism of the two substances. Of the material used in the following analyses, more than nine-tenths consisted of the yellow iodide of antimony; and as the results agree so closely both with theory and with the parallel analyses of the associated red iodide, which could be easily and perfectly isolated, there can be no question whatever that the two have the same percentage composition. These analyses are reproduced from our previous paper, in order to bring together all the facts bearing on the present discussion.

COMPARATIVE ANALYSES OF RED AND YELLOW IODIDE OF ANTIMONY.

Red Hexagonal.			Yellow Orthorhombic.		
No.	Weight taken.	% of Iodine.	No.	Weight taken.	% of Iodine.
1.	1.1877	76.110	1.	0.4610	76.161
2.	2.3201	76.040	2.	0.3496	76.161
	Mean value	76.075			76.161

Theory for SbI_3, when $Sb = 120$ and $I = 127$ 76.047

As additional evidence of the isomerism of these remarkable substances, we may here, in anticipation of a fuller discussion of the subject, mention a fact which would be by itself conclusive. At a very moderate elevation of temperature, the yellow iodide of antimony is completely converted into the red modification, and under such conditions that there can be neither loss nor gain of material in the process.

In measuring the angles of the rhombic plates as they lay in a normal position under the microscope, we found that we could obtain the sharpest results by projecting the image on a sheet of paper by means of a camera lucida. We were then able to adjust a straight edge to one after the other of two edges of the crystal, and draw the corresponding lines, whose angular divergence we then measured with a protractor. These measurements gave, for the acute angle of the

rhomb, as a constant result, 60°. The supplementary angles, 120°, are usually truncated; but not unfrequently (as shown on Plate III., Fig. 2) we meet with perfect terminations of this kind. When these occur on the same sprays as the acute angles, they uniformly appear in their proper relative positions, at right angles to the supplementary terminations, and we have frequently seen both terminations on the same rhombic plate. Less frequently, we find the sixty-degree angles truncated; and, as the result of such truncation, we have observed isolated hexagonal plates as perfect as those of the hexagonal iodide, from which outwardly they only differed in their color.

We have represented in Plate III., Fig. 1, a spray, presenting, for the most part, quite a different set of terminations from those before figured, which, although they are not quite so well defined as the others, nevertheless measure very constantly 82° and 98°. When found on the same sprays, the 98° terminations are, in general, parallel to the 60°, and the 82° to the 120°. Moreover, the 98° terminations are very frequently found bevelling the constantly recurring terminations of 60°, and, on the other hand, as often, the terminations of 120° bevel those of 82°.

Sometimes one of the two bevelling planes disappears, or, at least, is reduced to such small dimensions as to be imperceptible on the section as shown under the microscope. This kind of hemihedrism is shown, in the largest termination, both on Plates II. and III.

The angles 98° and 82°, or more accurately 98° 12′ 50″ and 81° 47′ 10″, are the angles of the rhombic prism {120}, derived from the prism {110} of 120° and 60°. The relation of these two prisms is shown by the figure below the drawing, on Plate II.; and it will be noticed that all the termination edges in the drawing are parallel to one or the other of the lines whose relative positions are thus defined. It is a very remarkable property of the prism of 120°, that the derived prisms {120} and {230} have identically the same angles; the only difference being that the relative positions of these angles (98° 13′ and 81° 47′) are reversed. This is shown in the same figure as before, where the prism {230} is also represented, but by dotted lines. The property referred to depends on the circumstance, that one-half and two-thirds of the tangent of 60° $\left(\frac{\sqrt{3}}{2} \text{ and } \frac{2}{\sqrt{3}}\right)$ are reciprocals, and must therefore be the tangent and cotangent of the same angle, which is 40° 53′ 35″, or one-half of the prismatic angle 81° 47′ 10″ named above. The same values are also equal, respectively, to the sine and cosecant of 60°, or to the cosine and secant of 30°. Not only,

therefore, is the rhombic prism of 81° 47′ in either of the positions we have described, crystallographically compatible with the prism of 120°; but also the two diagonals of the first bear to each other precisely the same relation which the lateral axes of a direct hexagonal prism or rhombohedron bear to those of the corresponding inverse forms.

The prism 81° 47′ evidently corresponds to the prism of approximately the same dimensions, on the crystals of antimonious bromide {101}, Fig. 3, Plate I.; and this new condition of antimonious iodide is therefore closely isomorphous with the only known state of antimonious bromide and antimonious chloride.

The rhombic plates of the yellow iodide are quite uniformly marked parallel to the edges and sides of the rhomb, showing an evident tendency to the formation of domes and octahedrons, — a phenomenon so familiar in skeleton crystals.

Although the habit and grouping of the new crystals, the dimensions of their angles, and their relations to known forms, furnish very satisfactory evidence of their orthorhombic character, yet, from the nature of the case, this evidence is not demonstrative, and we were therefore desirous of obtaining the more conclusive evidence which optical characters give. The crystals, however, obtained as we have described, are usually so excessively thin that we were obliged to search a long time before we could find single plates sufficiently thick to give a distinct interference image. We did, however, at last obtain several plates which enabled us to observe all the important features of this instructive phenomenon. The hyperbolas were well marked, and separated by about six divisions of the scale of Groth's polariscope, which corresponds to an apparent angle between the optical axes of about 36°, although, on account of the thinness of the plate and consequent indefiniteness of the boundaries of the images, it was impossible to measure the angle exactly. The acute bisectrix was perpendicular to the faces of the plate, at least as closely as could be observed; the dispersion of the axes was very marked; and the hyperbolas were bordered with green on the concave and red on the convex side. Hence, $\rho > v$. No differences could be seen in the coloration between the two ends or the two sides of the image. A very perfect isolated hexagonal plate enabled us to determine that the plane of the optical axes was parallel to the sides of the hexagon, as in most micas, and as represented in Fig. 4. This plate was not sufficiently

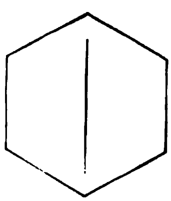


Fig. 4.

thick to show the hyperbolas distinctly; but, by combining it with a plate of a negative uniaxial crystal (tourmaline), we readily obtained the same familiar modification of the interference figure which is produced by a very thin plate of mica, and we were thus able, not only to determine that the character of the double refraction of our yellow plate was negative, but also to fix the position of the plane of the optical axes as just described.

We have stated that, at a very moderate temperature, the orthorhombic iodide changes to the hexagonal. It is now important to describe this remarkable phenomenon in detail. The change is not a gradual one; but suddenly, as soon as the required temperature is reached, a red spot appears, generally at one end of the rhombic plate, and then the red color rapidly spreads through the crystal, so that at any one point the change is instantaneous. Again, the change is attended with no disintegration of the crystal or loss of transparency; and not only the outline, but also all the minute markings, remain afterwards as sharp as before. Externally, there is simply a change of color from greenish yellow to bright red; and, by sudden cooling, it is perfectly easy to arrest the change so as to leave one part of the crystal red, while the rest remains yellow. The change, however, is attended with an entire alteration of structure; for the optically biaxial rhombic plate suddenly becomes absolutely uniaxial. Under the polarizing microscope, this change produces a very striking effect. In the dark field between crossed Nicols, the green rhombic plates show, of course, brilliant colors, whenever the diagonals of the rhomb lie obliquely to the planes of polarization; but, when the change takes place, a dark shadow suddenly spreads over each crystal, extinguishing this color, and then, on removing the analyzer, the very brilliant red color which the crystals have acquired appears. Under the polariscope, the sudden change from a biaxial to a perfectly uniaxial interference figure is still more striking. We have represented in Plate II. this remarkable phenomenon, as nearly as possible with a chromo-lithograph. The colors imitate very nearly, although not exactly, those of the natural crystals.

It becomes now a very interesting point to ascertain what is the exact temperature at which this singular change takes place. For this purpose, we heated on watch-glasses small quantities of the yellow crystals to different regulated temperatures, by means of a small air-bath; and in each experiment the temperature was maintained constant, at the selected point, for at least fifteen minutes. Thus we observed in one series of successive experiments: —

After heating to 120°, complete change.
" " " 107°, no change.
" " " 110° " "
" " " 111° " "
" " " 112° " "
" " " 114°, partial change.
" " " 114° complete "

These results were completely confirmed by similar experiments, all of which indicated that 114° is very closely the temperature at which the change first begins; and this result is in complete accordance with the fact we have before stated, that the red iodide of antimony, when sublimed below 114°, is completely converted into the yellow modification.

It is evident, from the above experiments, that the point of the change we have been discussing is fully as sharply marked as the melting point of a solid; and, by referring to the table of melting points on page 84, it will be seen that 114° (the temperature at which the change takes place) is the very point at which, theoretically, the normal iodide of antimony ought to melt. Evidently, then, the yellow orthorhombic iodide does undergo incipient fusion at this point; and the molecules, becoming thus free to move, regroup themselves, and the more stable structure of the red hexagonal iodide results.

Here, then, we have certainly a most remarkable confirmation of the theory we have advanced in regard to the molecular structure of hexagonal forms. The two isomers we have just described have enabled us to show that absolutely the same external form is compatible with the differences of structure which distinguish the orthorhombic from the hexagonal system; and this fact, only probable before, is now demonstrated. Secondly, the conditions under which one of these isomers changes into the other indicates clearly that the difference between the two substances is simply a difference of grouping of the same molecules, and also that in the red modification the molecules are more intimately united than in the yellow. When we attempt to go further, and explain what this more intimate grouping is, we of course soon enter the region of theory; but the analogy furnished by the superimposed mica plates is certainly very strong. We may now be said to know that the structure of an hexagonal crystal can be produced by a more intimate grouping of the molecules of an orthorhombic crystal, whenever the dimensions are such that the same external form is compatible with these two types of internal structure. We also know that the

optical effect thus produced is like that obtained by superposing orthorhombic plates in a definite way. We further know, that, so long as these plates are kept of equal thickness, and their relative position maintained, the character of the effect is independent of their magnitude. Were the plates indefinitely thin and indefinitely small, there can be no question that a proportional effect would result, which, if indefinitely multiplied by passing the light through a great number of such superposed bundles, must give the same total effect as that obtained from a single bundle of thicker and larger plates. Now, molecules, in the sense in which we have used the term in connection with the theory we are discussing, are simply the elements of a certain definite orthorhombic structure, and have their analogues in small orthorhombic plates, — of mica, for example. By grouping these plates in a definite way, a certain optical effect is produced, without any change of external form. Precisely the same effect is the result of a change caused by heat in the mass of another orthorhombic material having the same crystalline form as the mica plates. Moreover, this change takes place at the exact temperature at which the parts of our protean material must acquire freedom of motion; and the obvious conclusion is, that in this change the elements of the orthorhombic crystal group themselves anew in the same way in which we group the mica plates in order to obtain a similar result. This is the outline of our argument. To enforce it, we have accessory facts, which show that the theory is in harmony with the accepted principles of polar forces and molecular mechanics, but these it is unnecessary to recapitulate. Of course, demonstration in such a case is out of the question; but we hope that we have been able to make clear that the theory of molecular macling, when stripped of the accessories which the conventional term "molecule" implies, is a close induction from the observed facts.

We have only one further point to make, before concluding the discussion of this portion of our subject. The color of the rhombic iodide of antimony is, as we have said, greenish yellow, recalling that of uranium glass; and, when either the yellow or the red iodide is dissolved in disulphide of carbon, the resulting solution has always the greenish yellow color of the first. In this solution, according to all theories, the molecules must be isolated; and the fact that this characteristic color is retained by the rhombic structure, and wholly changed in the hexagonal, is additional evidence that, while in the first the molecules act on the light as units, in the second their individual action must be modified by conditions depending on a peculiar mode of association.

Monoclinic or Clinorhombic Antimonious Iodide.

We have stated in the previous article, that, when a solution of antimonious iodide in carbonic disulphide is exposed to the atmospheric air under the influence of the solar light, the compound in solution undergoes a gradual oxidation, iodine is set free, and oxi-iodide of antimony is precipitated. If, after this action has continued for twelve or fourteen hours in the direct sunlight, the very dark colored solution is distilled over a water bath (at a temperature which, even at the end of the process, should not exceed the boiling point of the solvent), the greater part of the free iodine passes over with the distillate; and, by repeating the distillation several times after adding more of the solvent to the residue in the retort, almost the whole of the free iodine can be removed. When now the residue is again dissolved in the same solvent, and the solution is allowed to evaporate spontaneously, there is generally deposited, at first, a crop of the crystals of the red hexagonal iodide; but, on decanting the remaining solution, we obtained, as a final result, a small amount of yellow monoclinic crystals similar to the one figured on Plate I. Fig. 6. These represent a third condition of antimonious iodide, which, being more soluble in disulphide of carbon, are very easily separated from the hexagonal iodide with which they are associated.

The yield of monoclinic crystals in the process we have described is uncertain and irregular; and as yet we have been unable to bring the conditions of their formation wholly under command. After much experimenting, however, we have reached a few definite conclusions. To the crystals prepared as above, there frequently adhered a perceptible amount of free iodine, and we naturally questioned whether this impurity might not have some influence on their production; but after repeatedly recrystallizing the hexagonal iodide from solutions containing even a large excess of free iodine, and obtaining none of the monoclinic modification, we concluded that the iodine had no further effect than to modify the habit of the hexagonal crystals as already described on page 78. In like manner, finding in certain cases, when crude disulphide of carbon was used, that the yield of monoclinic crystals was unusually large, we at once suspected that the impurities originally existing in the solvent might be the determining cause of the change of conditions in the crystals deposited from it. We therefore experimented with some very strong-smelling disulphide of carbon which had become yellow by long exposure to light and air; but we could not obtain the monoclinic crystals, except in uncertain

traces, until the disulphide with the dissolved iodide of antimony was exposed to the direct sun-rays for a long time, as above described. An equal amount of exposure before dissolving the iodide had no apparent effect. Again, after finding that iodide of antimony dissolved in disulphide of carbon is oxidized by ozonized air even in the dark, we sought to determine whether the monoclinic crystals were formed under these conditions independent of the action of the light; and, to this question also, our experiments returned a negative answer.

The production of the monoclinic crystals appears, therefore, to be independent of the oxidation of the iodide of antimony; although, like the latter, it is also due to the action of the sunlight. The effect seems to depend on a change produced in the solvent by the sun's rays, probably the same partial reduction of the carbonic disulphide which has been studied by O. Loew.* At least, it is certain that the monoclinic crystals contain a small amount of carbonaceous impurity, which they acquire from the solvent; and our theory is, that, under the action of the light, the crystalline molecules become as it were loaded by the adhesion of this material, and that the monoclinic habit is due to this circumstance. It may be mentioned, in this connection, that when the monoclinic crystals are redissolved in carbonic disulphide, and recrystallized, only a small part of the material, as a rule, retains the monclinic form, the rest appearing in the more stable hexagonal condition. Still, there is a certain persistency of the new condition which would be natural with such a molecular adhesion as our theory assumes; and the remarkable adhesiveness of the material which is deposited by disulphide of carbon under the influence of the light is worthy of notice in this connection. Other facts bearing on this theory can be more intelligently discussed after this new form has been described.

The specific gravity of the monoclinic iodide of antimony was determined in the same way as that of the hexagonal modification (page 83), and with the following results: —

SPECIFIC GRAVITY OF MONOCLINIC ANTIMONIOUS IODIDE.

No.	Weight taken.	Sp. Gr. at 22°.
1.	1.2434	4.786
2.	2.2605	4.750
Mean value	. . . .	4.768

* Am. Journal of Science (2), xlvi. 363, and xli. 251.

It will be remembered that the mean value from five determinations of the specific gravity of the hexagonal modification was 4.848.

We made two analyses of the monoclinic iodide, each with a different preparation, and the iodine was determined as described in our previous paper. The small amount of impurity which would not dissolve in the tartaric acid solution was estimated in the first analysis, but not in the second, and we therefore give in each case the per cent of iodine in the crystals as they were weighed.

ANALYSES OF MONOCLINIC ANTIMONIOUS IODIDE.

No	Weight taken.	Weight of Ag. I obtained.	% of Iodine.
1.	1.3087	1.8332	75.73
2.	1.8988	2.6605	75.70
Mean value			75.715
Theory when Sb = 120 and I = 127			76.047

The insoluble residue in the material of the first analysis weighed two and one-half milligrammes; and, were allowance made for this impurity, the corresponding percentage of iodine would be raised to 75.87. We found, however, that this material, like the hexagonal modification when crystallized from the same solvent, contained a trace of oxi-iodide of antimony, which of course must also be taken into the account before we can expect a close agreement with theory. So far as our analyses indicate, the total amount of impurity in the monoclinic crystals is not greater than that which we often find in the hexagonal crystals when crystallized, like the first, from a solution in carbonic disulphide. The difference seems to depend on the condition in which the impurity is present: and the conception we have formed is, that in the first case the impurity is a mere admixture like dirt entangled by the crystalline structure, while in the last case it actually adheres to the molecules. This molecular adhesion is induced by the action of the light; and our theory assumes, that, while the primitive molecules thus loaded are prevented from macling, so as to produce the triads of the hexagonal structure as shown in Fig. 1, so, also, these loaded molecules, when united in the normal way as shown in Fig. 2, form a crystal differing essentially, although still not very widely, from the now familiar orthorhombic prism of sixty and one hundred and twenty degrees.

The perfect isomerism of the monoclinic crystals with the other forms of antimonious iodide is shown by the readiness with which they change into the hexagonal iodide even more strikingly than by the above analyses. The general color of these crystals, like that of the orthorhomic crystals, is yellow; but the shade of color varies considerably under different circumstances, depending obviously on the impurity present. The purest crystals we have obtained had the same green tinge as the orthorhombic plates represented by Plate II., although less pronounced; and from this the tint varied through lemon yellow to quite dark brown, the brownish tinge evidently resulting from the free iodine, which, as we have said, frequently adheres to the crystals. Now, when heated, the monoclinic crystals (like the orthorhombic plates) acquire a red color and hexagonal structure at a temperature below that at which they melt. But the point of the change is by no means so definite as in the former case; and we observed circumstances connected with it obviously depending on the impurities present, which have an important bearing on the theory we have advanced above.

In the first place, we found that the yellow monoclinic crystals would bear a temperature of from 120° to 125°, without undergoing change. The experiments were conducted like those with the orthorhombic crystals already described (page 90); and comparative experiments were made in which the two modifications were heated side by side. The orthorhombic crystals were uniformly converted into the red modification at 114°, while the monoclinic were only slowly altered even at 125°. Of one experiment, we have the note, Some yellow crystals remain after heating for half an hour at 125°; and of another, The change is gradual: the color deepens; the crystals become opaque, and soon after melt.

On the other hand, we observed that brownish crystals, which had been deposited from a solution containing a large excess of iodine, often reddened at the boiling point of water. In one experiment, in order to obtain a direct comparison, we heated for one hour side by side in a steam bath, portions of the following three different preparations:—

1. Greenish yellow orthorhombic plates obtained by sublimation.
2. Lemon yellow monoclinic crystals similar to the one figured on Plate I. Fig. 6.
3. Brownish monoclinic crystals evidently occluding free iodine.

Except the loss of evaporation, both 1 and 2 underwent no change, but 3 was wholly converted into the red modification. The change

was attended with some efflorescence, and the crystals generally became more or less opaque; but sometimes they retained their transparency quite perfectly, and we noticed instances in which the change spread through these crystals as through the orthorhombic plates before described. It is evidently the same change in both cases; and the best explanation we can give of the phenomena is, that, while the fixed carbonaceous occlusion, by loading the molecules, renders them less mobile, and thus tends to prevent the change, the volatile iodine, on the other hand, in breaking away from its attachment, destroys the unstable equilibrium of the molecules, and thus induces the change at a lower temperature than it would otherwise take place.

The habit of the clinorhombic or monoclinic crystals of antimonious iodide varies considerably under different conditions between prismatic and tabular forms. As in the case of the hexagonal iodide, the presence of an excess of iodine in the solution seems to determine the production of elongated prisms, while, after the solution has been freed from iodine, more tabular crystals are deposited. We measured numerous angles on crystals of these different types; and although the forms were obviously the same, and the similar angles very nearly equal, yet we observed differences in these angles amounting to fully half a degree, even when the several measurements must have been accurate to a minute. Such a variation in the angles was to be expected under the circumstances, and is wholly in harmony with the theory we have formed of the structure of these crystals. The crystal figured on Plate I. Fig. 6, and whose dimensions are given below, was selected from the product of the most successful crystallization we have yet made. On it were united all the forms we have observed on any of the crystals of this modification of antimonious iodide. It had a lemon yellow color, and was obviously of the tabular type. The crystal was very perfect, and most of the angles admitted of accurate measurement. The results are given below. They were verified by numerous repetitions of the measurements in zones and by comparison with similar angles measured on other crystals of the same preparation. As usual, we deduced the elements of the crystal from the measured values of three selected angles; and it will be noticed that the measurements of the other angles agree very closely with the values calculated from these data assumed to be fundamental. Indeed, we have seldom obtained better results with artificial crystals.

Crystalline Form of Antimonious Iodide.

Monoclinic Variety.

Forms {001}, {110}, {210}, {011}, {211}

Fig. 6, Plate I.

Fundamental Angles.

Between normals of	210 and $2\bar{1}0$	measured	75° 21′
" " "	001 " 210	"	105° 30′
" " "	001 " 211	"	53° 50′

Angle of Axes 70° 16′
Clinodiagonal, $\acute{a}$ = 1.6408
Orthodiagonal, $\dot{b}$ = 1.
Vertical, $\dot{c}$ = 0.6682

	Measured.	Calculated.
Between normals of 100 and 210	37° 40½′	37° 40½′
" " " 210 " 110	19° 24′	19° 24′
" " " 110 " $\bar{1}10$	65° 51′	65° 51′
" " " 001 " 110	100° 36′	100° 34½′
" " " 211 " $2\bar{1}1$	61° 37′	61° 36′
" " " 011 " $01\bar{1}$		115° 40′

Angle between basal edges made by {001} and {210}	100° 16′
" " " " " {001} " {110}	62° 44′

Basal edge angle at end of clinodiagonal	100° 16′	corresponds to the prismatic angle	104° 39′
Do.	62° 44′	do.	65° 51′

Vertical axis on the assumption that the forms {001} and {211} are orthorhombic 0.867

The crystals have a very well defined cleavage, parallel to the basal plane.

We endeavored to supplement the above crystallographic measurements by a study of the optical characters of the crystals; but, unfor-

tunately, in their natural state, these crystals were not well adapted to the purpose, and the best we have hitherto obtained have been too small, and the material too easily altered, to admit of the preparation of sections. We shall return to this work at the first opportunity, and we hope for better success in the future. For the present, we can only say that the axes of elasticity in the plane of symmetry make a small angle with the basal plane and its normal. With a minute and imperfect section, the rough measures which were alone possible under the microscope gave for the value of this angle about 8°. And, further, that we were unable to see the interference figure through the basal planes under conditions which were far more favorable than those under which the hyperbolas were seen through the orthorhombic plates: for the tabular monoclinic crystals we used in these observations were both larger and thicker than the plates; and, in order to secure an accurate comparison we examined the different crystals in succession. We also examined several cleavage sections parallel to the basal planes, with no better success; probably because the angle between the optical axes is sufficiently great to determine total reflection. The high index of refraction of the substance would naturally produce this effect at a very moderate value of the optical angle, and unfortunately the crystals at once lost their transparency when immersed in the liquids generally used in such cases.

The above results, although partial, are important as indicating a marked difference between the two classes of crystals we have last studied. Nevertheless, a comparison of measurements will show that the dimensions of the *basal section* of the monoclinic crystals differ by only two or three degrees from those of the orthorhombic plates before described. Thus, we have 62° 44′ in place of 60°, and 100° 16′ in place of 98° 13′; and if, from the angle of the hemi-octahedral plane on the basal section, we calculate the length of an assumed rectangular vertical axis, the value obtained (0.867) does not differ very greatly from the values of the corresponding axis for the chloride, bromide, and hexagonal iodide of antimony, as given on page 113. Moreover, on recrystallizing the monoclinic iodide from a solution in pure sulphide of carbon, we have in two instances obtained — mixed with the hexagonal iodide, which is always the chief product — microscopic rhombic plates showing all the planes of the octahedron, and whose angles (as nearly as they could be measured under the microscope) were 60° and 120°.

As it seems to us, the natural inference from the facts we have developed is the theory already intimated. According to this theory,

the monoclinic differs chemically from the orthorhombic iodide, only in containing a small amount of impurity. The molecules are supposed to be similarly constituted and similarly grouped together; but, by the adhesion of the impurity to the molecules, a certain difference of form results. This difference, although usually regarded as fundamental (for it is the difference between two crystalline systems), does not appear, as thus viewed, either great or essential; and the fact that similar differences of form are also met with in the mineral kingdom, among the micas, the vermiculites, and the chlorites, without the corresponding differences of chemical composition and physical qualities which an essentially different crystalline structure would imply, tends to sustain our theory. The subject is obviously one of great importance, and we may hope that the further study of these artificial products may serve to elucidate what has been a very obscure chapter in the science of mineralogy. We propose to continue the investigation, and as soon as larger and better crystals of the several conditions of antimonious iodide can be prepared, we shall repeat and complete the optical measurements. Meanwhile, we are studying the allied iodides, which promise further results. Every one who has had experience with this kind of work knows how easily an observer may fall into error by mistaking in these optical phenomena the delicate shades or features on which important distinctions frequently depend, and this is especially true when, as in the present case, the conditions are not the most favorable. An examination of larger and more perfect crystals will undoubtedly correct some of our data, and may modify some of our conclusions. The results here given are the best that could be obtained with the material at our command, and must be regarded as provisional until better material can be secured.

Tschermak maintains that the Muscovite micas are monoclinic crystals, of which the acute bisectrix makes a very small angle with the plane of cleavage; and it is possible that the crystals of antimonious chloride, bromide, and iodide, which we have studied, should partake of a similar structure; and that the thin, rhombic plates of antimonious iodide obtained by sublimation should differ from the monoclinic crystals of the same compound only in their habit. At least, with our present imperfect measurements, we cannot disprove such a theory; although the not necessarily incompatible theory advanced above seems to us the more probable of the two, and the only one which is consistent with the facts as they at present appear. Yet, if the other view should prove to be the more correct, the general result of the discussion in this paper would not be affected: only we must extend also

to such monoclinic crystals as we have described the principles here illustrated in regard to the relations of hexagonal forms.

The chlorites, the vermiculites, and the micas, whose crystallographic relations first suggested to us the theory of molecular macling, which the new facts developed in this paper have so fully confirmed, are all foliated minerals, of whose crystals the optical axis or acute bisectrix is either normal, or inclined at only a small angle to the plane of easy cleavage. With the crystals of antimonious iodide, both hexagonal and monoclinic, there is also an easy cleavage, parallel to the basal plane; and there is also a similar, if not an identical, relation of the optical axes. There is, however, no other evidence of a foliated structure, nor any sign of interlamination, such as we observed in those minerals. The crystals appear to be perfectly homogeneous, and (saving their great brittleness) cleave more like crystals of topaz than those of mica. The difference between the effect of interlamination and that which, as we suppose, results from molecular macling, must not be overlooked, although the optical phenomena in the two cases are so similar. What we called, in our paper on the vermiculites, interlaminar macling does not involve any essential change in the substance of the mineral; but molecular macling produces a new, although isomeric, substance. The red and the yellow antimonious iodides are as different substances as calcite and arragonite; and, as we conceive, the difference in the two cases is of the same kind.

The facts developed in this paper all point to a more intimate relation between the different crystalline systems than has generally been supposed to exist, and are in complete harmony with the opinion we have frequently expressed, — that differences of crystalline system are not necessarily more fundamental than corresponding differences of dimension in the same system.

Antimonious Oxi-Iodides ($SbOI$ and $Sb_4O_5I_2$).

We have already, page 92, described the very remarkable chemical reaction which takes place when a solution of antimonious iodide in carbonic disulphide is exposed to the action of light and air. The reaction is chiefly that expressed by the formula, —

$$SbI_3 + O = SbOI + I\text{-}I;$$

but this is, to a very limited extent, accompanied by the more complex reaction, —

$$4\ SbI_3 + O_5 = Sb_4O_5I_2 + 5\ I\text{-}I.$$

The oxi-iodides of antimony, being insoluble in carbonic disulphide, are precipitated as an amorphous yellow powder, while the free iodine remaining in the solution changes its original greenish yellow color to a deep red, so deep that it soon appears black by reflected light. The change of color in the direct sunlight is very rapid, and forms a most striking phenomenon, which can readily be shown on the lecture table. When the direct rays of the sun are not available, the reaction can be produced by burning a few feet of magnesium ribbon. It is by far the most striking example of oxidation by the sun's light which has yet been discovered; and may, therefore, as a lecture experiment, be brought in striking contrast with the reduction of argentic chloride by the same agent, — a change which it rivals in extent, if not in rapidity. It has been maintained * that while the more refrangible rays of the solar spectrum exert a reducing action on metallic compounds, both binaries and salts, the less refrangible rays (the yellow as well as the red) produce the contrary effect, and tend to increase the oxidizing action of the atmosphere. In the phenomenon we are studying, the oxidation is actually determined by the sun's light, and in the most marked manner; and, as this is the first definite example of such action which has been observed, it became a very interesting question to inquire, in what part of the solar spectrum the action was most intense. We therefore exposed the solution, in test-tubes, to the sun's rays at different parts of the solar spectrum, but under otherwise identical conditions; taking care, of course, to protect the tubes from any other radiation. The spectrum was projected in the usual way, with a lense and prism of glass; and we found that, while the brilliant red and yellow rays caused no sensible change of color, the comparatively faint blue and violet rays produced a very marked effect. Our method of experimenting was not delicate enough to show the precise point of maximum effect; but it was evident that the whole order of the phenomena was the same as in the case of argentic chloride and similar photographic preparations.

As we have before stated, the solution of iodide of antimony undergoes no change in contact with ordinary air, so long as it is kept in the dark; and since the amount of iodine set free under the influence of the light can be readily estimated, and since this is the measure of the chemical action, it is evident that the new reaction affords a direct

* Étude sur la Part de la Lumière dans les Actions Chimiques, et en particulier dans les Oxydations par M. P. Chastaing. Annales de Chimie et de Physique (5), XI. 145. June, 1877.

means of measuring the amount of chemical change caused by solar radiation.

We have also stated, that, even in the dark, iodide of antimony is oxidized by ozone. The experiment is easily made by passing through the disulphide of carbon solution a current of air which has been ozonized by electricity. The action is very marked, but not so rapid as in the direct sunlight. The products are the same in both cases, — oxi-iodide of antimony and free iodine; and, under the influence of the sun's direct rays, all the iodide of antimony can be thus, with time, removed from the solution.

The reaction we are considering was first observed in a closed flask, and the circumstances were such that we did not at first suspect the important part which the atmospheric air played in the process. This however, became evident as soon as we had examined the products of the reaction; and we then made experiments to determine whether any reaction would take place out of contact with the air. For this purpose, we sealed up the solution in flasks from which the air had been displaced by carbonic dioxide, and, under these conditions, exposed the solution to the direct sun's light. But, although it was easy in this way to preclude any considerable change, we did not succeed in preventing it altogether. A slight reddening and turbidity indicated at least the beginning of oxidation, and this we traced to the oxygen gas held in solution by carbonic disulphide. But, after this small amount was exhausted, the action was wholly arrested, though we exposed the solution for days to the brightest sunlight.

Carbonic disulphide obviously aids the reaction by dissolving oxygen gas, as well as antimonious iodide; but we must not overlook what we stated in the previous paper, — that the same oxidation may take place independently of this solvent. The crystals of antimonious iodide, the yellow as well as the red, soon become coated with oxi-iodide, when exposed to the light and air; and we have lost a number of fine specimens from this cause. Under the microscope, the oxi-iodide appears as a yellow efflorescence, which soon destroys the transparency of the mass; and the odor of free iodine can be perceived on opening the bottle in which the preparation has been kept. This action, of course, is comparatively slow, but not less definite than that which we have been previously considering.

The oxi-iodide which, during oxidation, falls from the solution of antimonious iodide, is an amorphous yellow or brownish yellow powder. As it is insoluble in carbonic disulphide, it can easily be separated and cleaned by filtration and washing with this liquid. We made analyses of three different preparations, with the following results: —

ANALYSES OF ANTIMONIOUS OXI-IODIDE.

No.	Weight taken.	Weight of AgI obtained.	% of Iodine.
1.	0.1105	0.0837	40.94
2.	0.5728	0.4511	42.56
3.	0.2411	0.2059	46.15
		Theory for SbOI	48.29
		" " $Sb_4O_5I_2$	31.20

Whence it is evident that the material consists chiefly of SbOI; and, by regulating the action, this substance can be thus obtained in a nearly pure condition, as the last analysis shows.

The chemical constitution of the precipitated oxi-iodide is also very plainly indicated by the successive changes which it undergoes when heated in an atmosphere of inert gas, especially if they are studied in connection with the precisely similar changes which the well crystallized, and therefore more definite, oxichloride of antimony (SbOCl) undergoes under the same conditions as already described, page 63, of this volume. We experimented on the oxi-iodide with the apparatus also described and figured in our previous paper; and we found that, from the dried precipitate, when heated in a current of carbonic dioxide gas, antimonious iodide begins to sublime at 150°. At 200°, the sublimation became active, and continued until a definite amount of SbI_3 has been driven off, when it wholly ceased. In external appearance, the residue differed only slightly from the original substance; but when analyzed it gave the following result:—

Analysis of residue after heating at 200°, until sublimation ceased.

Weight taken.	Weight of AgI obtained.	% of Iodine.
1.8853	1.1512	32.99

On now heating the residue more intensely, it underwent no further change until the temperature rose above 350°; but, at a low red heat, antimonious iodide again sublimed, and there was left, as the final residue, beautifully crystallized antimonious oxide — both orthorhombic prisms and octahedrons. The reactions were obviously these:—

$$\text{At } 200°, 5\,SbOI = Sb_4O_5I_2 + SbI_3.$$

$$\text{At low red heat, } 3\,Sb_4O_5I_2 = 5\,Sb_2O_3 + 2\,SbI_3.$$

On examining the residue of the last reaction, before the change was complete, we have observed, mixed with the very brilliant colorless crystals of antimonious oxide, faintly yellow crystals, which had a well-marked monoclinic form, resembling that of the crystals of antimonious oxichloride ($Sb_4O_5Cl_2$); which are deposited from aqueous solutions of antimonious chloride which contains a deficiency of tartaric acid, and which we shall describe hereafter. These crystals were only microscopic objects, and far too small both in size and quantity for chemical analysis or crystallographic measurement. We were, however, able to prove, both that they contained iodine, and that they were converted into Sb_2O_3, on further heating; and there can be, therefore, no question that they were crystallized, $Sb_4O_5I_2$.

Antimonious Oxibromides (SbOBr and $Sb_4O_5Br_2$).

Under the influence of the air and the direct sunlight, a solution of antimonious bromide undergoes a slow oxidation like that we have just studied, but to a far less extent. Bromine is set free, and an oxibromide of antimony is deposited in an amorphous brownish powder; but the action is so slight, that, even after several weeks' exposure, we were unable to obtain, from a considerable volume of the solution, a sufficient amount of the precipitate for analysis. We were only able to prove that, like SbOI, it is decomposed when heated in two stages, leaving a residue of Sb_2O_3; but this reaction was sufficient to indicate that it consisted mainly, at least, of SbOBr. The precipitate contained a considerable amount of carbonaceous material, also separated from the solvent by the light; and it evidently owed its color to this impurity. Pure SbOBr would undoubtedly be colorless.

The compound $Sb_4O_5Br_2$ can readily be obtained, by heating in a sealed tube, to a temperature of 160°, a mixture of antimonious bromide and absolute alcohol, according to the method employed by Schaeffer* for preparing the oxichlorides. Some beautifully crystalline oxibromide has been recently prepared in this way by Mr. Clifford Richardson, a student of this laboratory. The crystals were distinctly monoclinic, although too small for measurement. Mr. Richardson's analysis gave the following result:—

* Berichte der Deutschen Chem. Gesell. 1868.

Analysis of Antimonious Oxibromide.

Prepared with Alcohol.

Weight taken.	Weight of AgBr obtained.	% of Bromine.
0.6634	0.3424	21.96
Theory for $Sb_4O_5Br_2$ when Sb = 120		22.22

Several attempts were made to prepare SbOBr, by using a larger proportion of antimonious bromide as compared with the alcohol, according to the indications furnished by Schaeffer's experiments with antimonious chloride; but the product was uniformly $Sb_4O_5Br_2$; nor have we been, as yet, more successful in isolating the compound in other ways.* An analysis of the white amorphous precipitate formed by the action of water on antimonious bromide showed that it also consisted essentially of the same, $Sb_4O_5Br_2$. The following result was obtained by Mr. Richardson: —

Analysis of Antimonious Oxibromide.

Precipitated by Water.

Weight taken.	Weight of AgBr obtained.	% of Bromide.
0.2281 gramme.	0.1155	21.54

Antimonious Oxichlorides (SbOCl and $Sb_4O_5Cl_2$).

These two compounds were prepared in a crystalline condition by following the directions given by Schaeffer in the paper already referred to. The crystals of SbOCl were not described by Schaeffer. Those obtained by Mr. Richardson were from half a millimetre to a millimetre in length, and enabled us to determine their crystallographic dimensions with approximate accuracy. They were evidently monoclinic, and presented the planes of an oblique rhombic prism with a klinodome and pinacoids.

* We also tried to prepare crystallized oxi-iodides of antimony by Schaeffer's method, but without success. A solution of antimonious iodide in absolute alcohol yields, without heating, an abundant precipitate of oxi-iodide, but as a perfectly amorphous powder. The material was evidently a mixture of the two oxi-iodides we have distinguished. Analysis gave for one preparation 46%, and for another 40.58%, of iodine.

Crystalline Form of Antimonious Oxichloride (SbOCl).

Prepared by Schaeffer's Method.

Monoclinic System.

Forms {110}, {011}, {001}

Fig. 7, Plate I.

Angles Measured.

Between normals, —

110 on $\bar{1}10$	98° 2′
011 „ $01\bar{1}$	107° 14′
110 „ 001	100° 8′
001 „ $\bar{1}\bar{1}0$	79° 52′

From these we calculated : —

Clinodiagonal, $\acute{a}$ = 0.8936
Orthodiagonal, b = 1
Vertical, $\dot{c}$ = 0.7587
Angle of Axes, = 76° 31′

By referring to page 97, it will be seen that these crystals are closely isomorphous with those of the monoclinic, antimonious iodide. We examined them also with a polarizing microscope, and found that, when the light passed normally to the prismatic faces, the principal optical sections made angles of 40° and 50°, respectively, with the prismatic edges.

The following analyses were made by Mr. Richardson. In the first three, the oxichloride was decomposed by boiling over it a solution of pure sodic carbonate. In the last, it was dissolved in a concentrated aqueous solution of tartaric acid.

Analyses of SbOCl.

Prepared by Schaeffer's Process.

No.	Weight taken.	Weight of AgCl obtained.	% of Chlorine.
1.	0.5055 gram.	0.4158 gram.	20.35
2.	0.7208 „	0.5997 „	20.41
3.	0.8367 „	0.6915 „	20.45
4.	0.5476 „	0.4488 „	20.28
	Mean value		20.37
	Theory Sb = 120		20.70

The want of closer agreement in the results, both with each other and with theory, we traced to a slight admixture of $Sb_4O_5Cl_2$; and we found that this last compound was by far the more readily formed of the two, and, except in the single experiment by which the preparation subsequently analyzed was obtained, the chief product of the reaction was largely mixed with the more oxygenated compound, even when the prescribed formula had been closely followed.

By operating with several hundred grammes of antimonious chloride and alcohol, we obtained the compound $Sb_4O_5Cl_2$ in beautiful large crystals, some of which were over a centimetre in length. We used for the purpose a cylindrical vessel of platinum, having a capacity of about 300 cubic centimetres; which, when covered with a lid of the same material, fitted exactly the interior of a Papin's digester, made nearly after the pattern recommended by Frankland.* This device was suggested by the "soda-water" fountains described on page 118 of the previous volume of these "Proceedings." The outside shell of such fountains must necessarily be very strong, and is now often made of steel plates; but the aerated water is held by an interior vessel, which, though independent of the shell, forms its lining. This inner vessel may be even of glass, for it bears no strain; since a small aperture through the neck equalizes the pressure on the outer and inner surfaces, and the "lining" fits the shell so tightly that no space is left into which the contents can overflow.

The general form of the crystals of $Sb_4O_5Cl_2$, prepared as we have described, is shown by Fig. 8, Plate I., and they are evidently more highly modified than those figured by Schaeffer. They are frequently terminated at the two ends, and usually differently terminated, as our drawing represents. At one end, we have an acute tetrahedral solid angle, formed by the meeting of the planes of a hemioctahedron with those of a vertical dome, while at the other end we have an edge formed by the meeting of the single basal plane with the single plane of an orthodome found on the crystal. These crystals thus present a very striking example of hemihedrism at the terminations, and we propose to examine hereafter their polar relations. The faces have a high vitreous lustre, and many of the angles can be measured with great precision. Unfortunately, however, but as a natural result of the multiplication of the octahedral planes, the faces of the principal prism are generally striated parallel to the basal intersections, and this striation renders more or less uncertain the measurements of the angles

* Watt's Dictionary of Chemistry, article *Bath*, i. 520.

between the octahedral and the prismatic faces, on which we had chiefly to depend for determining the position of the vertical axis. The value of the angle $\bar{1}12$ on $\bar{1}10$, which we selected as one of the fundamental data, was obtained by comparing a number of crystals on which the condition of the faces was especially favorable, and is the most probable value deduced from many observations. Nevertheless, this is the one doubtful element, and may be in error to the extent of a few minutes. The result was checked by measuring the angle of $\bar{1}12$ on 110, which, although not favorably situated as a measure of the fundamental dimensions of the crystal, was useful as a proof of the accuracy of the work by which they were deduced; and the table below shows how well it bears this test. As in this last measurement, the reflected image of the signal crossed the striations at nearly 90°, the signal was comparatively well defined; and the same was true in the measurements of the prismatic angles, which agreed very closely on different crystals. The hemioctahedral planes $\{\bar{1}12\}$ were by far the best developed of all the planes of this class; but we selected in preference, as the fundamental octahedron, a subordinate form $\{\bar{1}11\}$, to which the associated planes bore a simpler numerical relation. The planes $\{\bar{1}13\}$ were so small that the reflection of the signal was seen only by flashes. The planes $\{\bar{3}31\}$ were the best defined of an indefinite zone between $\{\bar{1}11\}$ and $\{\bar{1}10\}$; among which others, with still higher parameters, might have been doubtfully distinguished. We have previously called attention to similar zones of planes * with high but yet definite numerical ratios. They are by no means an exceptional phenomenon, and their crystallographic interpretation seems to us worthy of more attention than it has received. The result of our measurement is given in the following table:—

Crystalline Form of Antimonious Oxichloride ($Sb_4O_5Cl_2$).

Prepared by Schaeffer's Method.

Monoclinic System.

Forms $\{\bar{1}10\}$, $\{\bar{1}11\}$, $\{\bar{1}12\}$, $\{\bar{1}13\}$, $\{\bar{3}31\}$, σ $\{101\}$, σ $\{100\}$

Fig. 8, Plate I.

Fundamental Angles.

Between planes	$\bar{1}\bar{1}0$	and	$\bar{1}10$	86° 49′
„ „	$\bar{1}12$	„	$\bar{1}10$	156° 42′
„ „	$\bar{1}\bar{1}2$	„	$\bar{1}12$	112° 7′

* These Proceedings, vol. iii., page 87.

From these, we calculated —

Clinodiagonal, $\acute{a} = 1.239$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 3.082$
Angle of Axes, $C = 58° 38'$

ANGLES ARRANGED IN SERIES.

				Calculated.	Observed.
Between normals	$00\bar{1}$	and	$11\bar{2}$	45° 45′	45° 47′
,, ,,	$00\bar{1}$	,,	$11\bar{1}$	55° 50′	55° 53′
,, ,,	$00\bar{1}$	,,	$33\bar{1}$	64° 17′	
,, ,,	$00\bar{1}$	,,	110	69° 3′	68° 50′
,, ,,	$00\bar{1}$	,,	$\bar{1}0\bar{1}$	97° 54′	97° 33′
,, ,,	110	,,	$\bar{1}10$	86° 49′	86° 49′
,, ,,	110	,,	$\bar{3}31$	88° 47′	88° 38′
,, ,,	110	,,	$\bar{1}11$	92° 12′	
,, ,,	110	,,	$\bar{1}12$	96° 11′	96° 14′
,, ,,	110	,,	$\bar{1}13$	99° 12′	99° 2′
,, ,,	$\bar{1}\bar{1}3$	,,	$\bar{1}13$	57° 30′	
,, ,,	$\bar{1}\bar{1}2$	,,	$\bar{1}12$	67° 53′	67° 53′
,, ,,	$\bar{1}\bar{1}1$	,,	$\bar{1}11$	80° 9′	
,, ,,	$\bar{3}\bar{3}1$	,,	$\bar{3}31$	89° 2′	
,, ,,	$\bar{1}\bar{1}0$	,,	$\bar{1}10$	93° 11′	93° 11′
,, ,,	$\bar{1}10$	,,	$\bar{3}31$	4° 46′	
,, ,,	$\bar{1}10$	,,	$\bar{1}11$	13° 13′	
,, ,,	$\bar{1}10$	,,	$\bar{1}12$	23° 18′	23° 18′
,, ,,	$\bar{1}10$	,,	$\bar{1}13$	30° 52′	

We have not been able to study in detail the optical characters of these crystals; but observations with the polarizing microscope indicate, that, when resting on their prismatic planes, one of the principal optical sections is approximately, but not quite, parallel to the prismatic edges, making an angle with it of about 5°.

An analysis of the above crystals, made by Mr. Richardson, gave the following results: —

Analysis of Antimonious Oxichloride ($Sb_4O_5Cl_2$).

Prepared by Schaeffer's Process.

Weight taken.	Weight of AgCl obtained.	% of Chlorine.
0.6376	0.2879	11.17
Theory for $Sb_4O_5Cl_2$ when Sb = 120		11.25

We have already stated that this same compound is deposited from aqueous solutions of antimonious chloride containing less than a definite proportion of tartaric acid, under conditions which are given at length in our previous paper (page 23, of this volume). The crystals thus obtained differ wholly in general aspect from those we have just described. While the former were acicular, these are tabular, and, instead of being isolated, generally group themselves in tufts; which, although sometimes a millimetre in diameter, consist of crystals so small and so closely compacted together, that hitherto we have found it impracticable to separate and measure them. As seen under the microscope, the crystals appear distinctly monoclinic; the tufts presenting terminations similar to those of epidote, and the crystals showing the same tendency to growth in the direction of the orthodiagonal which is so characteristic of that mineral species; while, at the same time, the packing together of the tabular crystals in tufts recalls the phenomenon so familiar on specimens of calamine and prehnite. Assuming that the terminal planes at the ends of the orthodiagonal are the planes of a vertical prism, and the plane of twining the basal plane, then such rough estimates of the axial inclination as we have been able to make with the microscope would indicate that these crystals are much less oblique than the last, and more closely allied in form to the crystals of SbOCl before described. Like these, they frequently present the planes of a klinodome {011}, Fig. 7, Plate I., which never appear on the other type of crystals (Fig. 8), and indeed would hardly be compatible with it. By regulating more carefully the amount of tartaric acid in the solution, we hope to obtain hereafter larger crystals of this last variety of $Sb_4O_5Cl_2$, whose exact measurement will settle the question in regard to the relation of the two forms.

We analyzed with great care the crystals of $Sb_4O_5Cl_2$ deposited by the tartaric acid solution, in order to obtain additional evidence in regard to the atomic weight of antimony. By the methods already described, both the antimony and the chlorine were determined; while the oxygen was estimated, as is usual, by loss. The following are our results: —

ANALYSIS OF ANTIMONIOUS OXICHLORIDE ($Sb_4O_5Cl_2$).

CRYSTALLIZED FROM A TARTARIC-ACID SOLUTION.

	Found.	Theory.
Antimony . .	76.10	76.06
Chlorine . .	11.22	11.25
Oxygen . . .	12.68	12.68
	100.	100.

We also determined the specific gravity of these same crystals; which we found to be, at the ordinary temperature, 5.014.

OXICHLORIDE OF ANTIMONY ($Sb_8O_{11}Cl_2$).

As is well known, precipitated oxichloride of antimony (powder of Algaroth), when washed with hot water, undergoes a gradual decomposition; yielding after long-continued washing pure antimonious oxide, and hydrochloric acid, which is removed by the water. It is also known that, if the snow-white bulky precipitate is left under the liquid for a few days, it forms a grayish white mass, consisting of brilliant microscopic crystals, which are described by Johnston and Miller as oblique, rectangular prisms, having the obtuse summits replaced by planes. The amorphous precipitate is undoubtedly a mixture of the two compounds we have just studied, in varying proportions, depending on the conditions of the precipitation; but the crystals are evidently $Sb_4O_5Cl_2$. Johnston's analysis gives the exact theoretical per cent of chlorine (11.25); and the mean of two analyses by Peligot gives the same.* We can find no satisfactory evidence of a definite compound between SbOCl and $Sb_4O_5Cl_2$; and the fact that, when gradually heated, SbOCl manifests but one stage in its decomposition, seems to indicate that such a compound cannot exist. We have carefully studied this decomposition, and we would refer to the description of the phenomena which we gave in our previous paper, page 63, of this volume.† There

* Gmelin's Hand-book of Chemistry, Cavendish edition, iv. 367.

† The decomposition of the antimonious oxichlorides by heat, after the manner we have previously described, affords the finest crystals of Sb_2O_3 we have ever seen. These crystals are in part brilliant octahedrons (Seuarmontite), but chiefly orthorhombic prisms (Valentinite). The last are frequently highly modified, and terminated at both ends; affording an opportunity for a more complete crystallographic investigation of this substance.

was more probability that a definite compound might be isolated between $Sb_4O_5Cl_2$ and Sb_2O_3; and there is some evidence that such a compound had been analyzed.* With the hope of obtaining an intermediate product, we exposed to the direct sunlight during the summer months of 1876, a quantity of precipitated oxichloride of antimony, under a very large volume of water, which contained, besides the hydrochloric acid resulting from the decomposition of antimonious chloride, also a small quantity of tartaric acid. During this time there formed a considerable quantity of small acicular crystals, that were easily washed clean from the light amorphous precipitate with which they were mixed. The crystal appeared under the microscope perfectly homogeneous, and their surfaces had a brilliant vitreous lustre. They were rhombic prisms, having one of the two pairs of prismatic edges truncated by pinacoid planes. They presented, however, no distinctive terminations, sometimes tapering on the four prismatic planes to a point, and at other times on the pinacoids to an edge. They had the aspect of trimetric crystals, resembling some forms of Arragonite; and, as accurately as could be determined with the polarizing apparatus of a microscope, the principal optical sections were parallel to the prismatic edge, in whatever position the prisms might lie on the stage of the instrument. Nevertheless, these characters are not conclusive; and a delicate oblique striation which we observed on some of the prismatic planes led us to suspect that the crystals are really monoclinic. An analysis of the above crystals, made by Mr. Richardson, gave the following results: —

ANALYSIS OF ANTIMONIOUS OXICHLORIDE ($Sb_8O_{11}Cl_2$?).

No.	Weight taken.	Weight of AgCl obtained.	% of Chlorine.
1.	0.3605	0.0852	5.84
2.	0.7353	0.1759	5.91
		Mean value	5.875
		Theory for $Sb^8O^{11}Cl^2$	5.88

It is therefore probable that we have here the intermediate compound sought; although it is important that these observations should

* Gmelin's Hand-book of Chemistry, Cavendish edition, iv. 367.

be confirmed by further experiments. The assumed compound would be the second member of a possible series of oxichlorides, whose molecules each contain two atoms of chlorine, and of which the compound $Sb_2O_3Cl_2$ is the first term. In like manner, SbOCl is the first term of a parallel series, each of whose molecules contain one atom of chlorine, thus: —

OXICHLORIDES OF ANTIMONY.

$SbOCl$	$Sb_2O_2Cl_2$
Sb_3O_4Cl	$Sb_4O_5Cl_2$
Sb_5O_7Cl	$Sb_6O_8Cl_2$
$Sb_7O_{10}Cl$	$Sb_8O_{11}Cl_2$

This table suggests, not only that there is a possibility of forming other compounds of this class, but also that there may be among them several isomers. On the next page, we give a table which offers a general review of the crystallographic relations of the more important antimonious compounds.

Our object in this paper has been to put on record a very considerable number of new facts; and if, in presenting them in their philosophical relations, we have laid open numerous deficiencies in our knowledge which must be supplied by future investigation, we have only made evident, in the case of antimony, what is equally true of our knowledge of the chemical relations of many other equally common elementary substances. Some of these deficiencies we hope to be able to supply ourselves in future papers.

We would again express our obligations to the same gentlemen named at the close of the previous paper, for the assistance they have rendered in this portion of the investigation also. We are especially indebted to Dr. Gooch, for his aid in the crystallographic measurements; and to Mr. Oliver W. Huntington, for the drawings with which the paper is illustrated.

Comparison of Crystalline Forms of Antimonious Compounds.

Orthorhombic.

	Valentinite	Sb_2O_3
	Stibnite	Sb_2S_3
	Stibiozincite	Sb_2Zn_3
	Dyscrasite	$SbAg_3$
	Antimonious Chloride	$SbCl_3$
	Antimonious Bromide	$SbBr_3$
α	Antimonious Iodide	SbI_3

Hexagonal.

β	Antimonious Iodide	SbI_3

Monoclinic.

	Antimonious Oxisulphide	Sb_2OS_2
	Antimonious Oxichloride	$Sb_4O_5Cl_2$
	Antimonious Oxibromide	$Sb_4O_5Br_2$
	Antimonious Oxi-iodide	$Sb_4O_5I_2$
	Antimonious Oxichloride	$SbOCl$
γ	Antimonious Iodide	SbI_3

Plate I.

Fig. 1.

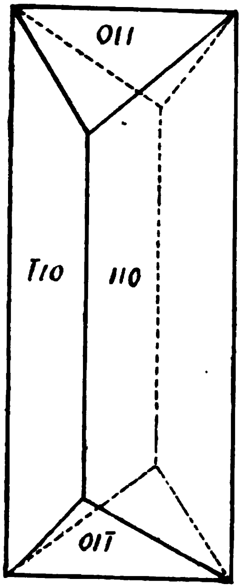


Fig. 2.

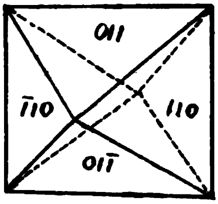


Fig. 8.

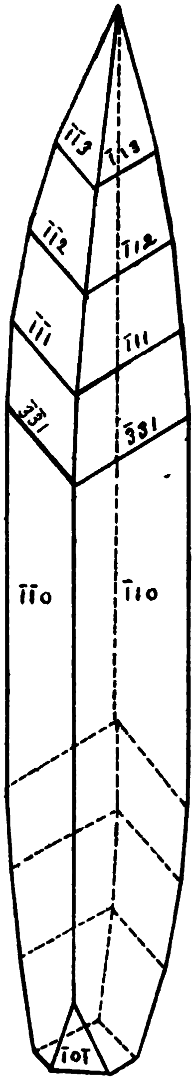


Fig. 7.

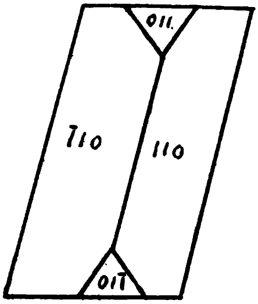


Fig. 3.

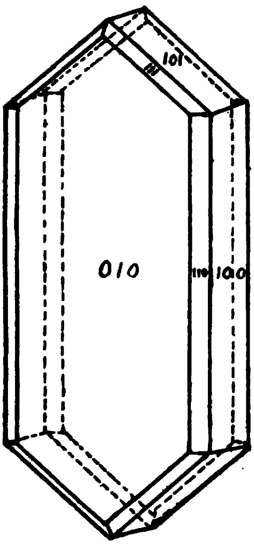


Fig. 5.

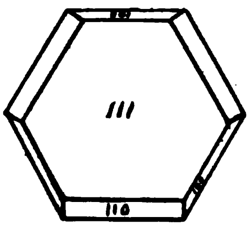


Fig. 6.

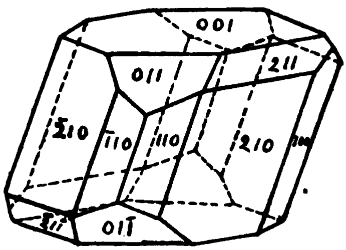


Fig. 4.

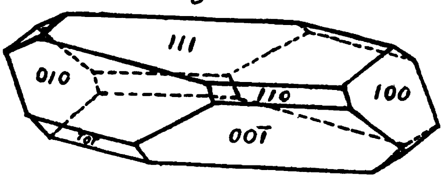
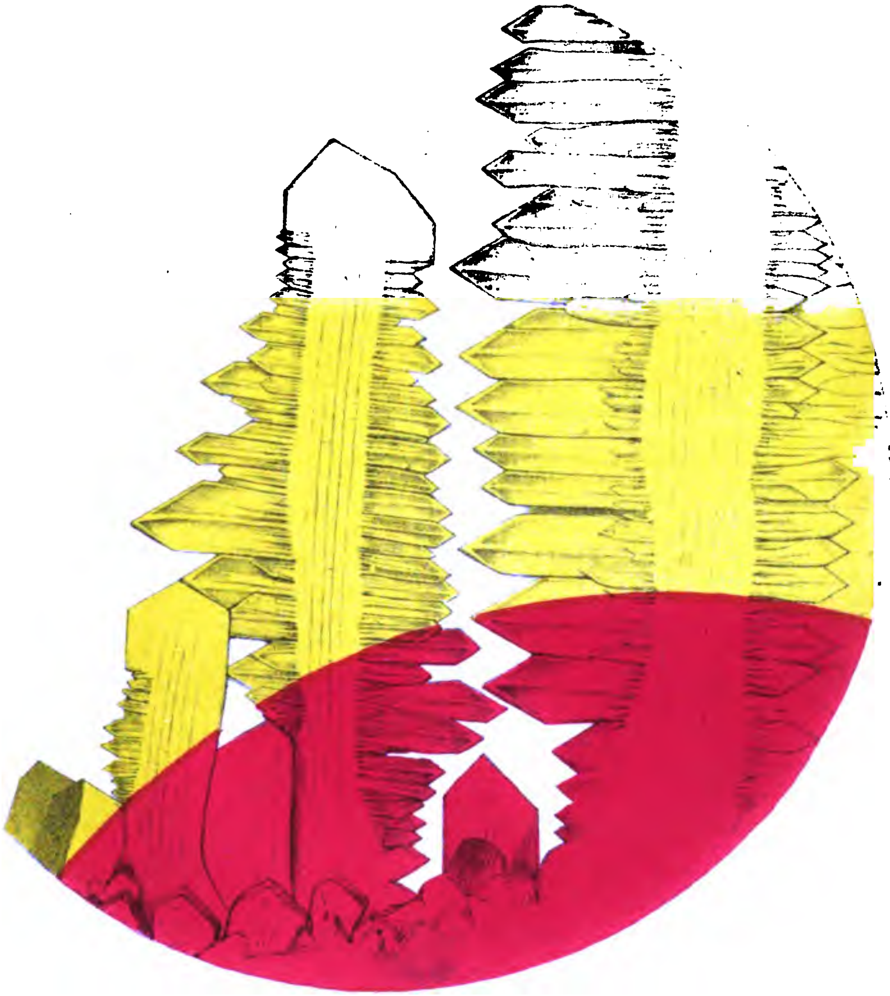


Plate II.



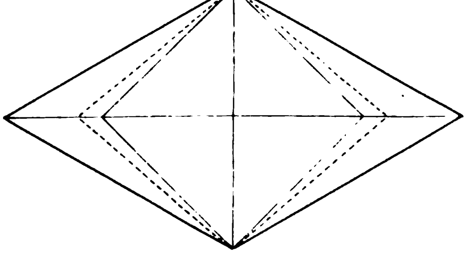


Plate III.

Fig. 1.

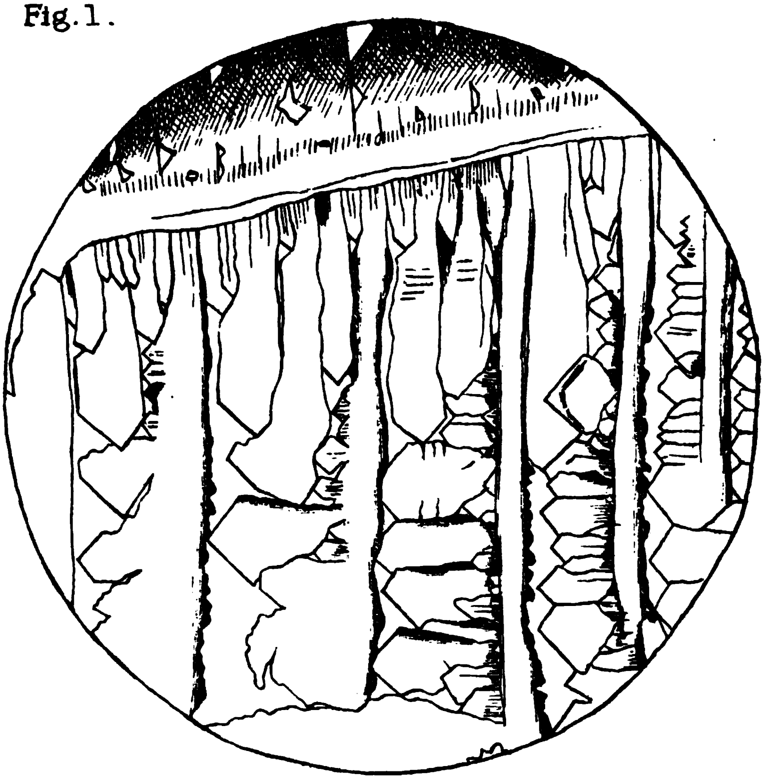
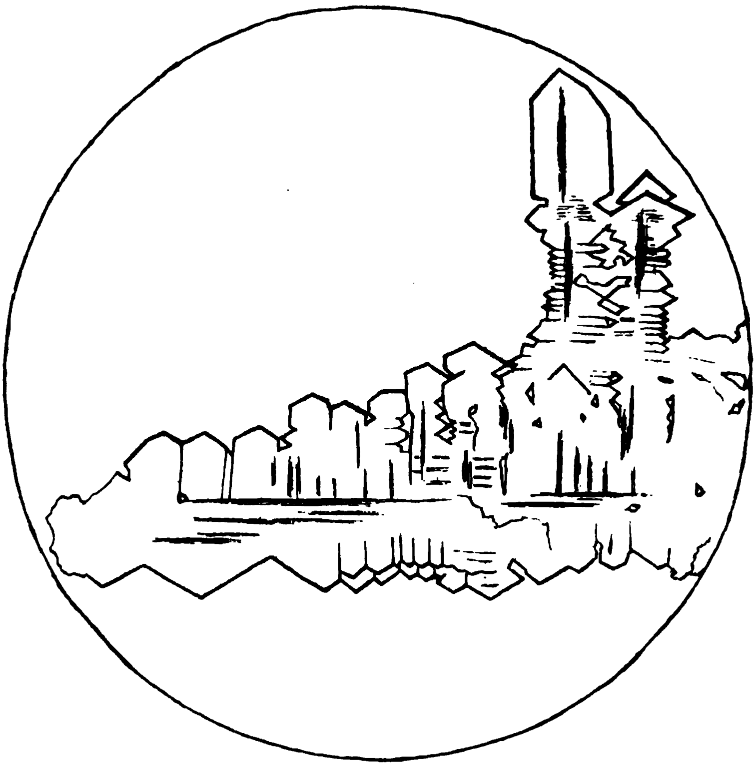


Fig. II.



XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE ATOMIC WEIGHT OF ANTIMONY.

PRELIMINARY NOTICE OF ADDITIONAL EXPERIMENTS.

By Josiah P. Cooke.
Erving Professor of Chemistry and Mineralogy.

Presented March 10, 1880.

In our previous paper on this subject,* we gave our reasons for the opinion, since fully confirmed, that the bromide of antimony is the most suitable compound of this element, as yet known, for determining its atomic weight; and the results of fifteen analyses of five different preparations of the bromide were published, which gave for the atomic weight in question the mean value 120.00 with an extreme variation between 119.4 and 120.4 for all the fifteen analyses, and between 119.6 and 120.3 for the six determinations in which we placed most confidence. The antimonious bromide used in these determinations was purified first by fractional distillation, and secondly by crystallization from a solution in sulphide of carbon. In the crystallized product thus obtained, the bromine was determined gravimetrically as bromide of silver in the usual way. Although it seemed at the time that the results were as accordant as the analytical process would yield under the unfavorable conditions, which the presence of a large amount of tartaric acid in the solution of the bromide of antimony necessarily involved; yet it was obvious that the agreement was far from that which was desirable in the determination of an atomic weight, and our chief confidence in the accuracy of the mean value —

* These Proceedings, Vol. XII. page 1.

independently of its remarkable agreement with previous results — was based on the fact that the known sources of error tended to balance each other. Hence our conclusions were stated with great caution, and the hope was expressed that after a more thorough investigation of the subject we might be able "to return to the problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible." Unfortunately this investigation has been delayed by causes beyond our control.

In our previous paper, we described a simple apparatus which we devised for subliming iodide of antimony; and in a note to the paper we stated that we were applying the same process to the preparation of the bromide of antimony, and that it promised excellent results. Our expectations in this respect have been fully realized, and the product leaves nothing to be desired either as regards the beauty or the constancy of the preparation. The fine acicular crystals are perfectly colorless, and have a most brilliant silky lustre. With ordinary precautions they can be kept indefinitely without change, and it is easy therefore to determine the weight of the material analyzed to the tenth of a milligramme.

We have carefully studied the causes of error involved in the analytical process of determining bromine in an aqueous solution of bromide of antimony and tartaric acid by the usual gravimetric method. These causes we propose to discuss in a future more extended paper. In this preliminary notice, we have only space to state that we have satisfied ourselves that the small differences between the results previously obtained arose wholly from the analytical process, and not from any want of constancy in the material analyzed; and further that these sources of error are to a very great extent under control. Moreover, we have found that the volumetric determination of bromine by silver was not materially affected, if at all, by the same causes. We have thus been led to devise a mode of testing the atomic weight of antimony, which, while it has all the advantages of the gravimetric method previously employed, is free from its sources of error.

If the atomic weight of antimony were 122.00, it would require 1.7900 grammes of pure silver to precipitate the bromine from a solution of 2.0000 grammes of antimony bromide, while if the atomic weight of antimony were 120.00 it would require 1.8000 grammes of silver. Now it is easy to estimate volumetrically $\frac{1}{100}$ of this difference with great certainty. We therefore prepared with great care

a button of *pure* metallic silver, which we annealed and rolled out to a thin ribbon. We then weighed out from two to four grammes of bromide of antimony, prepared by sublimation as described above, and dissolved this salt in an aqueous solution of tartaric acid, which we then transferred to a litre flask and diluted to about 500 cubic centimetres. We next very accurately weighed out a quantity of silver slightly less than that which calculation showed was required for complete precipitation. This silver was dissolved in nitric acid, and the solution having been evaporated to dryness over a water bath, the silver salt was washed into the flask containing the bromide of antimony. As soon as the supernatant liquid had cleared, the small additional amount of a normal silver solution required to produce complete precipitation was run in from a burette, and measured with the usual precautions. We used no extraneous indicator, because it was important not to introduce any possibly new disturbing element into the experiment, and in the titration of bromine with silver the normal and familiar phenomena, which mark the close of the process, furnish a very sharp indication. The details of one of the determinations were as follows: —

The weight of the bromide of antimony used amounted to 2.5032 grammes. To precipitate the bromine from the solution of this material 2.2404 grammes of silver would be required if Sb = 122.00 and 2.2529 if Sb = 120 00. We weighed out, with as much accuracy as if we were adjusting a weight, the smaller of these two quantities of metallic silver, and after dissolving the pure metal in pure nitric acid, evaporating the solution to dryness and redissolving in water, we added at once the whole of this silver solution to the litre flask containing the solution of bromide of antimony, in the manner described above. It was then found that $12\frac{4}{10}$ cubic centimetres of a normal silver solution (one gramme of silver to the litre) were required to complete the precipitation. It will be seen that the weights of the bromide of antimony and silver used could be thus determined with the most absolute precision, and we have the greatest confidence in these values to the $\frac{1}{10}$ of a milligramme. Moreover, it will be noticed that the volumetric method is only used to estimate the difference in the atomic weight which has been in question, and that if the method were only accurate to the $\frac{1}{10}$ of the quantity to be measured it would give us the value of the atomic weight within $\frac{2}{10}$ of a unit; while if, as we had reason to believe, the process was accurate within one per cent, it would fix the atomic weight within $\frac{2}{100}$ of a unit.

By the method just described, the following results were obtained. The letters *a* and *b* indicate different preparations.

Wt. of Sb Br_3 taken.	Total Wt. of Ag used.	Per Cent of Br Ag = 108 Br = 80.	Corresponding value of Sb.
a 1. 2.5032	2.2528	66.6643	120.01
a 2. 2.0567	1.8509	66.6620	120.02
a 3. 2.6512	2.3860	66.6644	120.01
b 4. 3.3053	2.9749	66.6696	119.98
b 5. 2.7495	2.4745	66.6653	120.01
Mean value,		66.6651	120.01
Mean value of fifteen gravimetric determinations previously published,		66.6665	
Theory Sb. 120 requires		66.6666	
„ Sb. 122 „		66.2983	

In order still further to control the work, we collected the bromide of silver formed in the last two determinations, washing the precipitate with the precautions which experience had shown to be necessary, and determining its weight, first, after drying at 150° C., and, secondly, after heating to incipient fusion. In *b* 6 there was a loss of $\frac{1}{10}$ of a millegramme; in *b* 7 a loss of $\frac{2}{10}$ of a millegramme only at the second weighing. This is an absolute proof that there could be no sensible occlusion of any tartaric acid or any tartrate by these precipitates, and, as stated in our original paper, the same test was frequently applied, although not always, in our previous determinations. It is also evident that these last experiments give us two essentially distinct determinations of the atomic weight, although the materials employed were identical with those of *b* 4 and *b* 5.

Wt. of Sb Br_3 taken.	Wt. of Ag Br determined.	Per cent of Bromine Ag = 108 Br = 80.	Corresponding value of Sb.
b 6. 3.3053	5.1782	66.665	120.01
b 7. 2.7495	4.3076	66.667	120.00
Mean value,		66.666	120.00

Lastly, it is obvious that these gravimetric determinations, taken in connection with the corresponding volumetric results, give us the most conclusive evidence of the purity, both of the metallic silver used, and

also of the bromine in the bromide of antimony, which is the basis of this atomic weight investigation. By comparing *b* 6 and *b* 7 with *b* 4 and *b* 5 respectively, we obtain the following data: —

1. 2.9749 gram. of silver gave 5.1782 gram. bromide of silver.
2. 2.4745 „ „ „ 4.3076 „ „ „

Hence it follows that, as shown by these experiments, the proportions of the silver to the bromine were respectively:—

	1.	108.00	Silver	to	79.99	Bromine.
	2.	108.00	„	„	80.01	„
Mean value,		108.00	„	„	80.00	„

This is the ratio of the atomic weight of silver to that of bromine, and corresponds to the second decimal place with the determinations of Stas as well as with those of Dumas.

In conclusion it gives us pleasure to express our obligations to Mr. G. De N. Hough and Mr. G. M. Hyams, two students of this laboratory, who have greatly aided us in the experimental work of this investigation.

[FROM THE AMERICAN JOURNAL OF SCIENCE, VOL. XIX, JUNE, 1880.]

ART. LXII.—*The Oxidation of Hydrochloric Acid Solutions of Antimony in the Atmosphere;* by JOSIAH P. COOKE. (Contributions from the Chemical Laboratory of Harvard College.)

IN our original paper on the Atomic Weight of Antimony—Proceedings of the American Academy of Arts and Sciences, vol. xiii, page 21—we made the following incidental observation in explanation of certain precautions which we found to be necessary in order to secure the precipitation of pure antimonious sulphide:

"The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air,—fully as rapidly as the solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air, if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grams of antimony."

On the sole basis of this language we have been represented as asserting that such antimony solutions oxidize in the air as rapidly as a solution of *ferrous chloride*, and experiments on comparatively dilute solutions of antimonious oxide in hydrochloric acid have been adduced as proofs that our observation was incorrect.

As is evident from the context, the statement just quoted, although the result of a very extended experience, was not based on quantitative measurements. What we noticed was that the solutions *were very quickly acted on* by the oxygen of the atmosphere, and we freely admit that the expression here italicized is a more accurate description of our observation, than the words originally used as quoted above. But our meaning was not left in doubt, for we expressly say immediately after, that the process is very slow and tedious. In regard to the phenomenon in question, the effects are so obvi-

ous when once attention is called to them, that it is entirely unnecessary to confirm our previous observations except so far as to add the following quantitative determinations, which will serve to give an accurate idea of the extent of the action under the only conditions we have investigated, or in regard to which we have written.

In order to determine the amount of oxidation caused by the action of the atmosphere on a solution of antimony in hydrochloric acid, we reduced the oxidized solution by boiling the liquid over antimony bullets, and determined the loss in their weight. This method is fully described in our original paper, and is based not only on the reducing power of the metal, but also on the fact repeatedly observed, that after the reduction was complete, the smallest excess of the finely pulverized metal would not dissolve even after prolonged boiling, and in the presence of a large excess of acid, if only the solution was protected from oxidation.

We began our experiments by dissolving 1·0036 grams of pure antimony (a portion of the same used in our experiments on the synthesis of antimonious sulphide) in about 30 cubic centimeters of pure hydrochloric acid (sp. gr. = 1·175) adding 3 cubic centimeters of very dilute nitric acid (containing only about 5·4 per cent of HNO_3). After the solution was completed we added bullets made of pure antimony (the same that had been used in our previous experiments), and boiled the solution in an atmosphere of carbonic dioxide, using the same apparatus which we described in our previous paper (loc. cit.) After the reduction was ended, the solution was transferred to a flat-bottomed flask through a platinum tunnel, on which the bullets were retained, and after washing into the flask the last traces of the solution with as small an amount of hydrochloric acid as possible, the tunnel was removed, the bullets washed with water, and again weighed as at first on the platinum tunnel. In reducing the original solution 0·4100 of a gram of antimony were dissolved from the bullets. The solution now containing 1·4136 grams of antimony was next exposed to the air for different successive periods of time in a room having a varying temperature of from 15° to 30°, sometimes in the shade, and at other times on a window seat where the sun's direct rays fell on the flask during several hours of each clear day.

We give in the following table the weight of antimony dissolved from the bullets after each successive exposure to the air; the amounts in each case being determined with all the precautions described above and still more at length in our former paper:

Weight of Sb originally dissolved............1·4136

1.	Dissolved from balls after 3 days' exposure,			0·0150	
2.	do. after 5 days'			0·0295	
3.	do.	" 10 "	May 17 to May 27,	0·0600	
4.	do.	" 23 "	May 27 to June 19,	0·1340	
5.	do.	" 37 "	June 19 to July 26,	0·2960	
6.	do.	" 120 "	July 26 to Dec. 24,	0·4481	0·9826

During these experiments the volume of the solution was gradually increased by the hydrochloric acid used in washing as above described, so that at last the volume amounted to 100 cubic centimeters.

It will be noticed that the amount of oxidation increased with the time of exposure, and that so long as the amount was small it was as nearly proportional to the time as could be expected under the varying conditions. The increased activity shown by determination No. 5 appeared to be due to the intensely warm weather and bright sunshine during the period, and the last determination would seem to indicate that after the oxidation reached a certain limit the process went on more slowly as we should naturally expect, but, with the greatly varying conditions during this long period, no certain conclusion can be drawn in regard to the effect of any single cause.

The action we are discussing is entirely in harmony with the chemical relations of antimony. The most striking characteristic of this elementary substance is its tendency to form compounds of the radical antimonyl, SbO. The oxichlorides, the oxibromides and the oxi-iodides whose relations we have discussed so fully in our previous papers, are examples in point, and we have been continually surprised by the appearance of such compounds in reactions in the most unexpected ways. In this respect antimony closely resembles vanadium, and with this element antimony is more closely allied than with its familiar associate, arsenic. What the precise reaction is in the present case, we are not prepared to state. That it is not the simple conversion of a terchloride into a pentachloride we are convinced, and investigations are in progress which we hope will further elucidate the subject.

In this connection we may appropriately add that while the above determinations were in progress we repeated the experiment described on page 19 of our previous paper (loc. cit.). We treated in an open flask 5 grams of finely powdered pure metallic antimony with 50 cubic centimeters of strong and pure hydrochloric acid, to which we added only one cubic centimeter of the very dilute nitric acid (5·4 per cent) described above. The flask was placed in a warm protected place (30° C.) and shaken from time to time. Soon the acid became col-

ored reddish-yellow and the chemical action began. When it had apparently ceased, the contents of the flask were shaken together, and the solution became at once as colorless as water. But on standing in the air the color rapidly returned, spreading from the surface of the liquid downward. These phenomena were repeated again and again during four or five months, until the whole of the metal dissolved. According to the reaction usually assumed to take place under these circumstances, 5 grams of metal would have required 50 cubic centimeters of acid, so that the effect was obtained with only one-fiftieth of the amount required by this theory.

[From the American Journal of Science, Vol. XIX, May, 1880.]

Art. LIV.—*On Argento-antimonious Tartrate* (*Silver Emetic*); by Josiah P. Cooke. (Contributions from the Chemical Laboratory of Harvard College).

As stated by us in our paper on the atomic weight of antimony,* this compound was originally obtained by Wallquist by precipitating nitrate of silver with tartar emetic, and was analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27·31 and 28·05 per cent of oxide of silver. They appear however to have prepared the substance only in an amorphous form. As stated in the paper just cited, we first noticed the formation of crystals of the compound in a concentrated solution of antimonious chloride and tartaric acid, to which had been added an excess of argentic nitrate, and from the circumstances of their formation we were led to form a somewhat erroneous inference in regard to their relation to water. We find that the substance is far more soluble in this solvent than at first appeared. We have found from further investigation that one part of silver emetic dissolves completely in one hundred parts of boiling and in somewhat less than five hundred parts of water at 15° C. In one determination made by evaporation, a saturated solution, which had stood a long time at a temperature of 15°, we found that 1000 parts of water had dissolved 2·76 parts and in another 2·68 parts of the salt. There is obviously therefore no danger of the formation of this product in the precipitation of chlorine, bromine or iodine from solutions of the antimony compounds of these elements in tartaric acid, unless the excess of silver nitrate is larger and the solutions concentrated; and although we have most carefully looked for it in the precipitate we have never discovered it, except under the peculiar conditions described in our former paper, and our fear that it might be occluded by these precipitates was wholly unfounded.

It is evident from the above experiments that the solubility of silver emetic in water like that of cream of tartar and other salts of tartaric acid is very greatly increased by heat, and we were easily able to obtain good crystals of the compound in large quantities by dissolving the precipitate, obtained as Wallquist describes, in boiling water, and allowing the solution to cool. The crystals are colorless and have a very brilliant, almost an adamantine, luster.

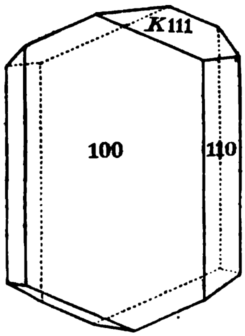
From the reaction by which silver emetic is formed we should infer that the composition of the salt would be expressed by the symbol

$$Ag, SbO, H_2 \equiv O_4 \equiv (C_4H_2O_2) \;.\; H_2O.$$

* This Journal, p. 382.

This compound would theoretically contain 26·34 p. c. of silver, and, as a mean of three analyses, we obtained for the amount of silver in the crystals 26·30 per cent, as previously stated.

The crystals of silver emetic rapidly blacken in the light and are very easily decomposed by heat. This decomposition takes place at about 200° C. with a slight explosion. A very fine carbon dust is blown out of the crucible and a residue is left behind, which under the microscope is seen to consist of spangles of metallic silver mixed with an amorphous powder. Almost the whole of the powder dissolved easily in a solution of tartaric acid, and it evidently consisted of Sb_2O_3. In one experiment we weighed the silver emetic and the product, and found that 0·8460 gram. of the salt left 0·5304 gram. of residue. If the residue consisted solely of silver and Sb_2O_3, theory would require 0·5200 grams, and it can be seen from this how perfect the decomposition was. It is obvious therefore that were this compound occluded as we at first feared, it would have made itself evident on drying the precipitates.



Mr. W. H. Melville, assistant in this laboratory, has made the following crystallographic measurements of the crystals whose formation and reactions we have described.

Angles between normals.

$(111) \wedge (100)$	70°	$19\frac{1}{8}'$
$(111) \wedge (\bar{1}11)$	70°	17′

$a : b : c = 1 : 1·386 : 0·571$

	I.	Measured.
100 110	54° 12′	54° 19′
$111 \wedge 110$	54° 51′	54° 54′

The pinacoid planes were irregular and the angles can only be regarded as approximate.

System Trimetric with hemihedral habit.

Observed planes $+ \varkappa$ | 111 | | 100 | | 110 | | 011 | ?

In the following table the crystallographic ratios are compared with those of the acid tartrates of rubidium, cæsium and potassium, formerly measured by us, and which have the same general form and hemihedral habit.

	Vertical.	Macro.	Brachy.
Acid tartrate of cæsium	0·661	1	0·694
Acid tartrate of rubidium	0·695	1	0·726
Acid tartrate of potassium	0·737	1	0·711
Silver emetic	0·412	1	0·721

[From the American Journal of Science, Vol. XXI, March, 1881.]

ON THE

SOLUBILITY OF CHLORIDE OF SILVER IN WATER.

By Josiah P. Cooke.

On the Solubility of Chloride of Silver in Water; by JOSIAH P. COOKE. (Contributions from the Chemical Laboratory of Harvard College.)

THIS subject has already been studied by Stas, whose observations are summed up by Dr. John Percy* in his recent volume on the Metallurgy of Silver in the following words:

"The solubility of the chloride is greatest when in the flaky state, as precipitated in the cold from a sufficiently dilute solution of silver; the solubility diminishes as the flakes shrink when left to themselves, or as they are rendered pulverulent by long agitation with water. Flaky or pulverulent chloride of silver, dissolved in water pure or acidified by nitric acid, is precipitated by the addition of a salt of silver or of hydrochloric acid or of an alkaline chloride." . . . "The solution of the chloride is wholly effected by pure or acidified water, as the case may be, and is not caused by the soluble salt formed simultaneously with the chloride of silver. The presence of nitric acid in the water does not affect the solubility of flaky chloride of silver; but it increases the solubility of the pulverulent chloride in proportion to the quantity of acid present. The precipitation of the dissolved chloride is the exclusive result of its insolubility in the solution formed by adding an excess either of the silver salt or of the alkaline chloride."

So also in Liebig and Kopp, Jahresbericht, 1871, 339: "According to Stas, the granular scaly and crystalline chloride is wholly insoluble in cold water: in boiling water the solubility is comparatively great, but decreases rapidly with the temperature."

In our investigation on the atomic weight of antimony we have had occasion to confirm and extend these observations of Stas, and our results may be of interest as showing that in the very familiar method of determining chlorine by precipitation with nitrate of silver, which is generally supposed to be extremely accurate, a sensible error may arise from the solubility of the chloride of silver in the hot distilled water used in washing the precipitate. It would be well for every analyst to make the following very striking experiment, which will enable him to appreciate the extent of the action in question.

Take from five to ten cubic centimeters of pure hydrochloric acid and precipitate the chlorine in the usual way with nitrate of silver, avoiding a large excess. After pouring off the supernatant liquid and washing the precipitate once or twice with cold distilled water, pour upon the white flaky chloride of silver a comparatively large volume of boiling water. As soon

* Metallurgy of Silver and Gold. Part 1, p. 60.

as the precipitate settles, pour off the clear hot water, dividing the solution between two precipitating jars. To one of these add a few drops of a solution of nitrate of silver, and to the other a few drops of hydrochloric acid. In both cases a precipitate of chloride of silver will fall, and most chemists, certainly, will be surprised at the effect; for it is not a mere turbidness that results, but a well-defined precipitate, whose amount is easily estimated. Successive portions of boiling water poured upon the precipitate give the same reaction. In one experiment the reaction was still perceptible in the fourteenth wash-water. But under the action of the boiling water, the precipitate becomes crystalline or granular and the action lessens, until at last the water does not dissolve sufficient chloride of silver to cause even a cloudiness on the addition of nitrate of silver, as just described. Mr. G. M. Hyams, a student in this laboratory, washed two different portions of chloride of silver with boiling water until the action ceased, and then weighed and examined the residue. In the first experiment, 1·4561 grams of chloride of silver were washed with 66 liters of water. The chloride of silver was then collected and found to weigh 1·2320 grams. Hence, 0·2241 grams, corresponding to 15·39 per cent had passed into solution. In the second experiment, 60 liters of water were used, and 16·03 per cent of the chloride of silver originally precipitated were dissolved. These numbers, however, are only approximately accurate, for as the precipitate becomes granular, it settles with less readiness, and there was necessarily some loss in filtering off so large a volume of liquid.

In the experiments above described the boiling water produced only a very slight decomposition of the chloride of silver. The precipitate, granulated by the washing, readily dissolved in aqua ammonia, leaving less than a milligram of a black powder, which was proved to be metallic silver.

The solvent power of water on freshly precipitated chloride of silver did not appear to be influenced by the presence of free nitric acid even in large quantities. We tried the effect both of dropping the nitric acid on the precipitate before pouring on hot water, and also of previously adding nitric acid to the boiling wash-water. We used amounts of nitric acid ($\delta = 1{\cdot}355$) varying from five to two hundred cubic centimeters to the liter of water, but without finding any marked difference in the result.

The presence of a small amount of nitrate of silver in the water entirely prevented its solvent action, so far as we could discover. In order to determine the limit of the action, we added different quantities of nitrate of silver to the boiling water before pouring it on to the precipitated chloride of silver. With one centigram of nitrate of silver to the liter of

water, there was a marked turbidness on subsequently adding an excess of the same reagent to the filtrate. With two, three, or even four centigrams to the liter, an opalescence could still be distinguished, although constantly diminishing with the increasing amount of the salt. With five centigrams, there was no opalescence, and we concluded that one decigram of nitrate of silver to the liter of boiling wash-water would certainly prevent all action.

A few drops of hydrochloric acid added to the wash-water greatly diminishes its solvent action on flaky chloride of silver, but does not wholly prevent it, as is evident from the fact shown in the table below, that hydrochloric acid does not precipitate chloride of silver from its solution in water nearly as effectually as nitrate of silver; and, as is well known, hydrochloric acid if in any considerable excess exerts a strong solvent action on the precipitated chloride.

As shown by Stas, the precipitation of chloride of silver from its solution in hot water by the reagents we have named, depends solely on the change which the reagents produce in the solvent. That the action is an example of simple solution is shown by the fact that a considerable portion of the chloride of silver dissolved in boiling water is deposited when the solvent cools. This phenomenon is a striking one and can easily be observed by pouring into a glass crystallizing pan some of the clear solution obtained in the experiment described above. As the water cools it becomes cloudy and deposits a granular powder which adheres to the bottom of the glass. The grains are usually very small, but if the solution cools slowly the crystalline form can readily be distinguished under the high powers of a good microscope, and the little cubes present all the characteristic of the native crystals of chloride of silver. It is evident, therefore, that the granular condition of chloride of silver is a crystalline condition, and this experiment may elucidate the manner in which the native crystals are produced.

We have thus far only spoken of the solubility of chloride of silver in boiling water. As is evident from the crystallization just described, the solubility rapidly diminishes as the temperature falls; but even at the ordinary temperature the solubility is distinctly marked. Luke-warm water poured on and off, freshly precipitated chloride silver becomes decidedly opalescent on the addition of nitrate of silver, and even if cold water is used the opalescence is perceptible.

In order to obtain an approximate measure of the effects we have described, Mr. Hyams precipitated about fifteen grams of chloride of silver, and, after thoroughly washing it, boiled the precipitate with a large volume of water in a glass flask.

At the end of an hour he decanted through a filter about one liter of the boiling water, and, having divided the filtrate into two portions, he added to one portion nitrate of silver, and to the other, hydrochloric acid. The precipitated chloride of silver was in each case collected and weighed. At the end of two hours' boiling, two other portions were filtered off and treated in a similar way. These determinations were then repeated with a fresh quantity of chloride of silver, and afterwards taking with a third quantity of chloride of silver, the boiling water was simply poured on twice in succession and the similar portions thus obtained treated as before. The results in every case were nearly the same as shown in the following table. In this table

1 and 3 are results after one hour's boiling of 1st quantity.
3 and 4 " " " two hours' " " " "
5 and 6 " " " one hour's " " 2d quantity, etc.
7 and 8 " " " two hours' " " " " "
9 and 10 after simply pouring on boiling water.
10 and 12 " " " " " "

No.	Wght. of Water.	Wght. of AgCl.	Wght. of AgCl per liter.	Precipitant.
1	523·6 gram.	0·0011	0·0021	Nitrate of silver.
2	469·5	0·0004	0·0009	Hydrochloric acid.
3	115·0	0·0002	0·0017	Nitrate of silver.
4	402·1	0·0004	0·0010	Hydrochloric acid.
5	225·0	0·0004	0·0018	Nitrate of silver.
6	462·0	0·0004	0·0009	Hydrochloric acid.
7	696·4	0·0014	0·0020	Nitrate of silver.
8	825·4	0·0007	0·0008	Hydrochloric acid.
9	700·4	0·0014	0·0020	Nitrate of silver.
10	747·2	0·0007	0·0009	Hydrochloric acid.
11	520·9	0·0011	0·0021	Nitrate of silver.
12	287·5	0·0003	0·0010	Hydrochloric acid.

If we assume that the amount of chloride of silver precipitated by nitrate of silver under the conditions described above is a correct measure of the solubility of the chloride, it appears from the above determinations that about two milligrams of chloride of silver are dissolved by each liter of boiling water, and further that only about one-half of the amount thus dissolved is precipitated by hydrochloric acid.

In making chlorine determinations it is a very common practice to wash with very hot water in order to secure the prompt settling of the chloride of silver or to wash away any occluded material, and it was the chief object of this investigation to determine the extent to which the solubility of the chloride in distilled water might effect the result. For this purpose we may make two series of determinations of the

chlorine in chloride of antimony; in both cases precipitating with nitrate of silver the chlorine from a solution of the chloride of antimony in tartaric acid and water with the usual precautions. But, while in the first series the precipitated chloride of silver was washed with boiling hot distilled water to about the $\frac{1}{100,000}$ according to Bunsen's scheme; in the second series although hot water was also used in washing, one decigram of nitrate of silver per liter was added to each successive portion of the wash-water poured upon the precipitate, until the last two portions, which were poured on cold. By this simple device the advantages of washing with hot water may be secured while its solvent action is prevented. The results are given in the following table.

FIRST SERIES.

No.	Weight of $SbCl_3$ taken.	Weight of AgCl obtained.	Per cent of Cl calculated.
1	2·3856 gram.	4·4784 gram.	46·441
2	3·1300	5·8712	46·407
3	3·4207	6·4243	46·462
4	5·0031	9·3790	46·377
		Mean value,	46·422
		Max. diff. from mean,	0·047

SECOND SERIES.

No.	Weight of $SbCl_3$ taken.	Weight of AgCl taken.	Per cent of Cl calculated.
1	3·4059 gram.	6·4188 gram.	46·624
2	3·6603	6·9014	46·643
3	2·4762	4·6658	46·617
4	2·5567	4·8212	46·651
		Mean value,	46·634
		Max diff. from mean,	0·017
	Difference between means of two series,		0·212

It is evident from these results that when great accuracy is required the solubility of chloride of silver may become a very serious source of error in determinations of chlorine, and in our investigation* of the atomic weight of antimony this was the chief cause of the discrepancy between the analyses of chloride of antimony on the one hand and the bromide, iodide and sulphide of antimony—analyses of which closely agreed among themselves—on the other hand. It was shown in the paper just referred to that, although the greatest care was taken in purifying the material, the chloride of antimony used actually left behind on evaporation a sufficient amount of oxichloride to reduce the per cent of chlorine 0·116.† The mean

* This Journal, III, xv, 41.

† This Journal, III, xv, 118.

results which we actually obtained from seventeen analyses of chloride of antimony was 46·620, and when to this we add 0·212 and 0·116 the sum is 46·948, which differs from 47·020—the theoretical value when Sb =120, and Cl =35·5—by only 0·072. In this estimate we leave out of the account the known solvent action on chloride of silver of the tartaric acid used to keep the antimony in solution. This must equally affect both of the series of determinations given above and fully accounts for the small difference that remains to be explained. This whole discussion, however, only serves to confirm the conclusion previously expressed, that chloride of antimony is a most unsuitable material for the basis of an atomic weight determination, and having explained the anomaly to which we gave prominence in a previous paper we shall here take leave of the subject. We have also studied the solubility of bromide of silver in water, but this is so small that we found it difficult to measure the amount. In water at the ordinary temperature, or even in tepid water, bromide of silver is practically insoluble. In boiling water it is perceptibly soluble but not more so than is chloride of silver in water at the ordinary temperature. Hence the determination of bromine does not require the same precautions and is susceptible of greater accuracy than that of chlorine; and on this account, as well as for other reasons which we have previously discussed, the atomic weight of antimony can be deduced from the analyses of the bromide of antimony with as great accuracy as can at present be reached in such determinations. In the seven determinations of the per cent of bromine in bromide of antimony which we have published,* the maximum difference from the mean value 66·6651 was only 0·0045, and Professor Mallet in his analyses of bromide of aluminum has obtained with the same method a similar degree of accuracy.†

In conclusion we would again express our obligations to Mr. G. M. Hyams, who has assisted us in the work of this investigation.

* This Journal, III, xix, 385.

† Philosophical Transactions, Part III, 1880, 1022.

PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XVII.

PAPERS READ BEFORE THE ACADEMY.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

By Josiah Parsons Cooke, *Director*.

Presented May 11, 1881.

Introduction.

In a paper presented to the Academy, and published in its proceedings, Vol. XIII., page 1, we gave the results of our investigation of the haloid compounds of antimony up to that time, including a revision of the atomic weight of this element. We did not directly answer the criticism which this paper called forth, except so far as to present to the Academy, March 10, 1880, and to publish in these Proceedings, Vol. XV., page 251, a preliminary notice of experiments then in progress which furnished the best possible answer to the unfounded assumptions of the critic. We also gave brief notices of our work from time to time in the American Journal of Science. But now that the work is ended for the present (or at least must be suspended for a considerable period), we propose to bring the results together in the present paper.

I. The Oxidation of Hydrochloric Acid Solutions of Antimony in the Atmosphere.

In our first paper (loc. cit., page 21) we made the following incidental observation, in explanation of certain precautions which we

found to be necessary in order to secure the precipitation of pure antimonious sulphide: —

"The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air, — fully as rapidly as the solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air. if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grammes of antimony."

On the sole basis of this language we have been represented as asserting that such antimony solutions oxidize in the air as rapidly as a solution of *ferrous chloride*, and experiments on comparatively dilute solutions of antimonious oxide in hydrochloric acid have been adduced as proofs that our observation was incorrect.

As is evident from the context, the statement just quoted, although the result of a very extended experience, was not based on quantitative measurements. What we noticed was that the solutions *were very quickly acted on* by the oxygen of the atmosphere, and we freely admit that the expression here italicized is a more accurate description of our observation than the words originally used as quoted above. But our meaning was not left in doubt, for we expressly say, immediately after, that the process is very slow and tedious. In regard to the phenomenon in question, the effects are so obvious, when once attention is called to them, that it is entirely unnecessary to confirm our previous observations except so far as to add the following quantitative determinations, which will serve to give an accurate idea of the extent of the action under the only conditions we have investigated, or in regard to which we have written.

In order to determine the amount of oxidation caused by the action of the atmosphere on a solution of antimony in hydrochloric acid, we

reduced the oxidized solution by boiling the liquid over antimony bullets, and determined the loss in their weight. This method is fully described in our original paper, and is based not only on the reducing power of the metal, but also on the fact repeatedly observed, that, after the reduction was complete, the smallest excess of the finely pulverized metal would not dissolve, even after prolonged boiling, and in the presence of a large excess of acid, if only the solution was protected from oxidation.

We began our experiments by dissolving 1.0036 grammes of pure antimony (a portion of the same used in our experiments on the synthesis of antimonious sulphide) in about 30 cubic centimetres of pure hydrochloric acid (sp. gr. = 1.175) adding 3 cubic centimetres of very dilute nitric acid (containing only about 5.4 per cent of HNO_3). After the solution was completed we added bullets made of pure antimony (the same that had been used in our previous experiments), and boiled the solution in an atmosphere of carbonic dioxide, using the same apparatus which we described in our previous paper (loc. cit.). After the reduction was ended, the solution was transferred to a flat-bottomed flask through a platinum tunnel, on which the bullets were retained; and, after washing into the flask the last traces of the solution, with as small an amount of hydrochloric acid as possible, the tunnel was removed, the bullets washed with water, and again weighed as at first on the platinum tunnel. In reducing the original solution, 0.4100 of a gramme of antimony were dissolved from the bullets. The solution now containing 1.4136 grammes of antimony was next exposed to the air for different successive periods of time in a room having a varying temperature of from 15° to 30°, sometimes in the shade, and at other times on a window seat, where the sun's direct rays fell on the flask during several hours of each clear day.

We give in the following table the weight of antimony dissolved from the bullets after each successive exposure to the air, the amounts in each case being determined with all the precautions described above, and still more at length in our former paper: —

Weight of Sb originally dissolved				1.4136	
1. Dissolved from balls after 3 days' exposure,				0.0150	
2. "	after 5 days			0.0295	
3. "	" 10	"	May 17 to May 27 .	0.0600	
4. "	" 23	"	May 27 to June 19 .	0.1340	
5. "	" 37	"	June 19 to July 26 .	0.2960	
6. "	" 120	"	July 26 to Dec. 24 .	0.4481	0.9826

During these experiments the volume of the solution was gradually increased by the hydrochloric acid used in washing as above described, so that at last the volume amounted to 100 cubic centimetres.

It will be noticed that the amount of oxidation increased with the time of exposure, and that, so long as the amount was small, it was as nearly proportional to the time as could be expected under the varying conditions. The increased activity shown by determination No. 5 appeared to be due to the intensely warm weather and bright sunshine during the period, and the last determination would seem to indicate that, after the oxidation reached a certain limit, the process went on more slowly, as we should naturally expect; but, with the greatly varying conditions during this long period, no certain conclusion can be drawn in regard to the effect of any single cause.

The action we are discussing is entirely in harmony with the chemical relations of antimony. The most striking characteristic of this elementary substance is its tendency to form compounds of the radical antimonyl, SbO. The oxichlorides, the oxibromides, and the oxiiodides, whose relations we have discussed so fully in our previous papers, are examples in point, and we have been continually surprised by the appearance of such compounds in reactions in the most unexpected ways. In this respect antimony closely resembles vanadium, and with this element antimony is more closely allied than with its familiar associate, arsenic. What the precise reaction is in the present case we are not prepared to state. That it is not the simple conversion of a terchloride into a pentachloride we are convinced; but, in order to elucidate the subject, further investigations are necessary.

In this connection we may appropriately add that while the above determinations were in progress we repeated the experiment described on page 19 of our previous paper (loc. cit.). We treated in an open flask 5 grammes of finely powdered pure metallic antimony with 50 cubic centimetres of strong and pure hydrochloric acid, to which we added only one cubic centimetre of the very dilute nitric acid (5.4 per cent) described above. The flask was placed in a warm, protected place (30° C.), and shaken from time to time. Soon the acid became colored reddish-yellow, and the chemical action began. When it had apparently ceased, the contents of the flask were shaken together, and the solution became at once as colorless as water; but, on standing in the air, the color rapidly returned, spreading from the surface of the liquid downward. These phenomena were repeated again and again during four or five months, until the whole of the metal dissolved. According to the reaction usually assumed to take place under these

circumstances, 5 grammes of metal would have required 50 cubic centimetres of acid, so that the effect was obtained with only one-fiftieth of the amount required by this theory.*

II. Argento-antimonious Tartrate (Silver Emetic).

On one occasion when analyzing antimonious chloride we noticed the formation of "silver emetic," and the observation led us to fear that this compound might be occluded by the argentic chloride or bromide, precipitated from a solution containing tartaric acid and antimony. This suspicion, thus excited, led us to make an investigation of the substance in question with the following results: —

As stated by us in our former paper, this compound was originally obtained by Wallquist by precipitating nitrate of silver with tartar-emetic, and was analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27.31 and 28.05 per cent of oxide of silver. They appear, however, to have prepared the substance only in an amorphous form. As stated in the paper just cited, we first noticed the formation of crystals of the compound in a concentrated solution of antimonious chloride and tartaric acid, to which had been added an excess of argentic nitrate, and from the circumstances of their formation we were led to form a somewhat erroneous inference in regard to their relation to water. We find that the substance is far more soluble in this solvent than at first appeared. We have found from further investigation that one part of silver emetic dissolves completely in one hundred parts of boiling, and in somewhat less than five hundred parts of water at 15° C. In one determination made by evaporating, a saturated solution, which had stood a long time at a temperature of 15°, we found that one thousand parts of water had dissolved 2.76 parts and in another 2.68 parts of the salt. There

* Although in our synthesis of antimonious sulphide it was our constant study from the first to prevent the oxidation of the product, and although we most carefully guarded every phase of the process, yet the theory was advanced that the apparent weight of the product was *increased* by a partial oxidation of the antimonious sulphide at the temperature at which the red was converted to the gray modification. In answer to this wholly gratuitous assumption, it is only necessary to say: 1. That the oxidation of the dried precipitate at this stage of the process is a well-marked phenomenon, with every phase of which we are acquainted. 2. That the oxidation is always attended with a *loss* of weight. 3. That the products of our determinations were always examined, and have been in two cases preserved, and that these do not show the least signs of oxidation.

is obviously therefore no danger of the formation of this product in the precipitation of chlorine, bromine, or iodine from solutions of the antimony compounds of these elements in tartaric acid, unless the excess of silver nitrate is very large and the solutions very concentrated; and although we have most carefully looked for it in the precipitate we have never discovered it, except under the peculiar conditions described in our former paper, and our fear that it might be occluded by these precipitates was wholly unfounded.

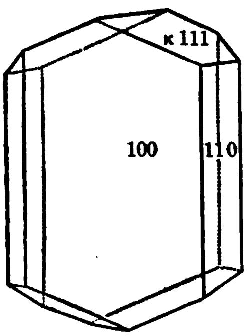
It is evident from the above experiments that the solubility of silver emetic in water like that of cream of tartar and other salts of tartaric acid is very greatly increased by heat, and we were easily able to obtain good crystals of the compound in large quantities by dissolving the precipitate, obtained as Wallquist describes, in boiling water, and allowing the solution to cool. The crystals are colorless and have a very brilliant, almost an adamantine, lustre.

From the reaction by which silver emetic is formed we should infer that the composition of the salt would be expressed by the symbol

$$Ag, SbO, H_2 \equiv O_4 \equiv (C_4H_2O_2) . H_2O.$$

This compound would theoretically contain 26.34 per cent of silver and, as a mean of three analyses, we obtained for the amount of silver in the crystals 26.30 per cent, as previously stated.

The crystals of silver emetic rapidly blacken in the light, and are very easily decomposed by heat. This decomposition takes place at about 200° C. with a slight explosion. A very fine carbon dust is blown out of the crucible, and a residue is left behind, which under the microscope is seen to consist of spangles of metallic silver mixed with an amorphous powder. Almost the whole of the powder dissolved easily in a solution of tartaric acid, and it evidently consisted of Sb_2O_3. In one experiment we weighed the silver emetic and the product, and found that 0.8460 gramme of the salt left 0.5304 gramme of residue. If the residue consisted solely of silver and Sb_2O_3, theory would require 0.5200 gramme, and it can be seen from this how perfect the decomposition was. It is obvious, therefore, that were this compound occluded as we at first feared, it would have made itself evident on drying the precipitates.



Mr. W. H. Melville, assistant in this laboratory, has made the fol-

lowing crystallographic measurements of the crystals whose formation and reactions we have described.

Angles between normals.

$(111) \wedge (100)$ 70° 19⅓′
$(111) \wedge (\bar{1}\bar{1}1)$ 70° 17′
$a : b : c = 1 : 1.386 : 0.571$

	I.	Measured.
100 ∧ 110	54° 12′	54° 19′
111 ∧ 110	54° 51′	54° 54′

The pinacoid planes were irregular and the angles can only be regarded as approximate.

System Trimetric with hemihedral habit.
Observed planes $+\kappa$ {111} {100} {110} {011} ?

In the following table the crystallographic ratios are compared with those of the acid tartrates of rubidium, cæsium and potassium, formerly measured by us, and which have the same general form and hemihedral habit.

	Vertical.	Macro.	Brachy.
Acid tartrate of cæsium . . .	0.661	1	0.694
" " rubidium . . .	0.695	1	0.726
" " potassium. . .	0.737	1	0.711
Silver emetic	0.412	1	0.721

III. On the Solubility of Argentic Chloride in Water.

In our analyses of antimonious chloride we constantly noticed, while washing the precipitated chloride of silver with warm water, that although the water first decanted from the precipitate was perfectly clear it became turbid when mixed with the successive washings; and on investigating the cause of this unexpected result we found that it was due to the chloride silver dissolved by the pure wash water and reprecipitated by the excess of nitrate of silver in the filtrate. As the solvent action of the water used for washing the precipitate evidently produced a marked effect on our chlorine determination, we determined at once to investigate the extent of the influence.

This subject has already been studied by Stas, whose observations are summed up by Dr. John Percy* in his recent volume on the Metallurgy of Silver in the following words:—

* Metallurgy of Silver and Gold, Part I. p. 60.

"The solubility of the chloride is greatest when in the flaky state, as precipitated in the cold from a sufficiently dilute solution of silver; the solubility diminishes as the flakes shrink when left to themselves, or as they are rendered pulverulent by long agitation with water. Flaky or pulverulent chloride of silver, dissolved in water, pure or acidified by nitric acid, is precipitated by the addition of a salt of silver, or of hydrochloric acid, or of an alkaline chloride. . . . The solution of the chloride is wholly effected by pure or acidified water, as the case may be, and is not caused by the soluble salt formed simultaneously with the chloride of silver. The presence of nitric acid in the water does not affect the solubility of flaky chloride of silver; but it increases the solubility of the pulverulent chloride in proportion to the quantity of acid present. The precipitation of the dissolved chloride is the exclusive result of its insolubility in the solution formed by adding an excess either of the silver salt or of the alkaline chloride."

So also in Liebig and Kopp, Jahresbericht, 1871, 339: "According to Stas, the granular scaly and crystalline chloride is wholly insoluble in cold water: in boiling water the solubility is comparatively great, but decreases rapidly with the temperature."

In our own investigation of this subject we have at once confirmed and extended these observations of Stas, and our results may be of interest as showing that in the very familiar method of determining chlorine by precipitation with nitrate of silver, which is generally supposed to be extremely accurate, a sensible error may arise from the solubility of the chloride of silver in the hot distilled water used in washing the precipitate. It would be well for every analyst to make the following very striking experiment, which will enable him to appreciate the extent of the action in question.

Take from five to ten cubic centimetres of pure hydrochloric acid, and precipitate the chlorine in the usual way with nitrate of silver, avoiding a large excess. After pouring off the supernatant liquid and washing the precipitate once or twice with cold distilled water, pour upon the white flaky chloride of silver a comparatively large volume of boiling water. As soon as the precipitate settles, pour off the clear hot water, dividing the solution between two precipitating jars. To one of these add a few drops of a solution of nitrate of silver, and to the other a few drops of hydrochloric acid. In both cases a precipitate of chloride of silver will fall, and most chemists, certainly, will be surprised at the effect; for it is not a mere turbidness that results, but a well-defined precipitate, whose amount is easily estimated. Successive portions of boiling water poured upon the precipitate give the

same reaction. In one experiment the reaction was still preceptible in the fourteenth wash-water. But under the action of the boiling water, the precipitate becomes crystalline or granular and the action lessens, until at last the water does not dissolve sufficient chloride of silver to cause even a cloudiness on the addition of nitrate of silver, as just described. Mr. G. M. Hyams, a student in this laboratory, washed two different portions of chloride of silver with boiling water until the action ceased, and then weighed and examined the residue. In the first experiment 1.4561 grammes of chloride of silver were washed with 66 litres of water. The chloride of silver was then collected, and found to weigh 1.2320 grammes. Hence, 0.2241 gramme, corresponding to 15.39 per cent, had passed into solution. In the second experiment 60 litres of water were used, and 16.03 per cent of the chloride of silver originally precipitated were dissolved. These numbers, however, are only approximately accurate; for, as the precipitate becomes granular, it settles with less readiness, and there was necessarily some loss in filtering off so large a volume of liquid.

In the experiments above described the boiling water produced only a very slight decomposition of the chloride of silver. The precipitate, granulated by the washing, readily dissolved in aqua ammonia, leaving less than a milligramme of a black powder, which was proved to be metallic silver.

The solvent power of water on freshly precipitated chloride of silver did not appear to be influenced by the presence of free nitric acid, even in large quantities. We tried the effect both of dropping the nitric acid on the precipitate before pouring on hot water, and also of previously adding nitric acid to the boiling wash-water. We used amounts of nitric acid ($\delta = 1.355$) varying from five to two hundred cubic centimetres to the litre of water, but without finding any marked difference in the result.

The presence of a small amount of nitrate of silver in the water entirely prevented its solvent action, so far as we could discover. In order to determine the limit of the action, we added different quantities of nitrate of silver to the boiling water before pouring it on to the precipitated chloride of silver. With one centigramme of nitrate of silver to the litre of water, there was a marked turbidness on subsequently adding an excess of the same reagent to the filtrate. With two, three, or even four centigrammes to the litre, an opalescence could still be distinguished, although constantly diminishing with the increasing amount of the salt. With five centigrammes, there was no opalescence, and we concluded that one decigramme of nitrate of

silver to the litre of boiling wash-water would certainly prevent all action.

A few drops of hydrochloric acid added to the wash-water greatly diminishes its solvent action on flaky chloride of silver, but does not wholly prevent it, as is evident from the fact shown in the table below, that hydrochloric acid does not precipitate chloride of silver from its solution in water nearly as effectually as nitrate of silver; and, as is well known, hydrochloric acid, if in any considerable excess, exerts a strong solvent action on the precipitated chloride.

As shown by Stas, the precipitation of chloride of silver, from its solution in hot water by the reagents we have named, depends solely on the change which the reagents produce in the solvent. That the action is an example of simple solution is shown by the fact that a considerable portion of the chloride of silver dissolved in boiling water is deposited when the solvent cools. This phenomenon is a striking one, and can easily be observed by pouring into a glass crystallizing pan some of the clear solution obtained in the experiment described above. As the water cools it becomes cloudy, and deposits a granular powder, which adheres to the bottom of the glass. The grains are usually very small; but if the solution cools slowly the crystalline form can readily be distinguished under the high powers of a good microscope, and the little cubes present all the characteristics of the native crystals of chloride of silver. It is evident, therefore, that the granular condition of chloride of silver is a crystalline condition, and this experiment may elucidate the manner in which the native crystals are produced.

We have thus far only spoken of the solubility of chloride of silver in boiling water. As is evident from the crystallization just described, the solubility rapidly diminishes as the temperature falls; but even at the ordinary temperature the solubility is distinctly marked. Luke-warm water poured on and off freshly precipitated chloride of silver, becomes decidedly opalescent on the addition of nitrate of silver, and even if cold water is used the opalescence is perceptible.

In order to obtain an approximate measure of the effects we have described, Mr. Hyams precipitated about fifteen grammes of chloride of silver, and, after thoroughly washing it, boiled the precipitate with a large volume of water in a glass flask. At the end of an hour he decanted through a filter about one litre of the boiling water, and, having divided the filtrate into two portions, he added to one portion nitrate of silver, and to the other, hydrochloric acid. The precipitated chloride of silver was in each case collected and weighed. At the end

of two hours' boiling, two other portions were filtered off and treated in a similar way. These determinations were then repeated with a fresh quantity of chloride of silver, and afterwards taking a third quantity of chloride of silver, the boiling water was simply poured on twice in succession, and the similar portions thus obtained treated as before. The results in every case were nearly the same as shown in the following table. In this table

1 and 2 are results after one hour's boiling of 1st quantity.
3 and 4 " " " two hours' " " " "
5 and 6 " " " one hour's " " 2d quantity, etc.
7 and 8 " " " two hours' " " " " "
9 and 10 after simply pouring on boiling water.
10 and 12 " " " " " "

No.	Wght of Water.	Wght of AgCl.	Wght of AgCl per litre.	Precipitant.
1	523.6 gram.	0.0011	0.0021	Nitrate of silver.
2	469.5	0.0004	0.0009	Hydrochloric acid.
3	115.0	0.0002	0.0017	Nitrate of silver.
4	402.1	0.0004	0.0010	Hydrochloric acid.
5	225.0	0.0004	0.0018	Nitrate of silver.
6	462.0	0.0004	0.0009	Hydrochloric acid.
7	696.4	0.0014	0.0020	Nitrate of silver.
8	825.4	0.0007	0.0008	Hydrochloric acid.
9	700.4	0.0014	0.0020	Nitrate of silver.
10	747.2	0.0007	0.0009	Hydrochloric acid.
11	520.9	0.0011	0.0021	Nitrate of silver.
12	287.5	0.0003	0.0010	Hydrochloric acid.

If we assume that the amount of chloride of silver precipitated by nitrate of silver under the conditions described above is a correct measure of the solubility of the chloride, it appears from the above determinations that about two milligrammes of chloride of silver are dissolved by each litre of boiling water, and further that only about one half of the amount thus dissolved is precipitated by hydrochloric acid.

In making chlorine determinations, it is a very common practice to wash with very hot water, in order to secure the prompt settling of the chloride of silver, or to wash away any occluded material, and it was the chief object of this investigation to determine the extent to which the solubility of the chloride in distilled water might affect the result. For this purpose we made two series of determinations

of the chlorine in chloride of antimony; in both cases precipitating with nitrate of silver the chlorine from a solution of the chloride of antimony in tartaric acid and water with the usual precautions. But, while in the first series the precipitated chloride of silver was washed with boiling hot distilled water to about the $\frac{1}{100.000}$ according to Bunsen's scheme; in the second series, although hot water was also used in washing, one decigramme of nitrate of silver per litre was added to each successive portion of the wash-water poured upon the precipitate, until the last two portions, which were poured on cold. By this simple device, the advantages of washing with hot water may be secured, while its solvent action is prevented. The results are given in the following table:—

FIRST SERIES.

No.	Weight of $SbCl_3$ taken.	Weight of AgCl obtained.	Per cent of Cl calculated.
1	2.3856 gram.	4.4784 gram.	46.441
2	3.1300	5.8712	46.407
3	3.4207	6.4243	46.462
4	5.0031	9.3790	46.377
		Mean value,	46.422
		Max. diff. from mean,	0.047

SECOND SERIES.

No.	Weight of $SbCl_3$ taken.	Weight of AgCl obtained.	Per cent of Cl calculated.
1	3.4059 gram.	6.4188 gram.	46.624
2	3.6603	6.9014	46.643
3	2.4762	4.6658	46.617
4	2.5567	4.8212	46.651
		Mean value,	46.634
		Max. diff. from mean,	0.017
	Difference between means of two series,		0.212

It is evident from these results that when great accuracy is required, the solubility of chloride of silver may become a very serious source of error in determinations of chlorine, and in our first paper on the atomic weight of antimony, this was the chief cause of the discrepancy between the analyses of chloride of antimony on the one hand, and the bromide, iodide, and sulphide of antimony — analyses of which closely agreed among themselves — on the other hand. It was shown in the paper just referred to that, although the greatest care was taken in purifying the material, the chloride of antimony used actually left

behind on evaporation a sufficient amount of oxichloride to reduce the per cent of chlorine 0.116 (loc. cit. page 64). The mean results which we actually obtained from seventeen analyses of chloride of antimony was 46.620; and when to this we add 0.212 and 0.116, the sum is 46.948, which differs from 46.985 — the theoretical value when $Sb = 120$, and $Cl = 35.457$ — by only 0.037, or if we take $Cl = 35.5$ by 0.072. In this estimate we leave out of the account the known solvent action on chloride of silver of the tartaric acid used to keep the antimony in solution. This must equally affect both of the series of determinations given above, and fully accounts for the small difference that remains to be explained. This whole discussion, however, only serves to confirm the conclusion previously expressed, that chloride of antimony is a most unsuitable material for the basis of an atomic weight determination; and, having explained the anomaly to which we gave prominence in a previous paper, we shall here take leave of the subject. We have also studied the solubility of bromide of silver in water, but this is so small that we found it difficult to measure the amount. In water at the ordinary temperature, or even in tepid water, bromide of silver is practically insoluble. In boiling water it is perceptibly soluble, but not more so than is chloride of silver in water at the ordinary temperature. Hence the determination of bromine does not require the same precautions, and is susceptible of greater accuracy than that of chlorine; and on this account, as well as for other reasons which we have previously discussed, the atomic weight of antimony can be deduced from the analyses of the bromide of antimony with as great accuracy as can at present be reached in such determinations. In the seven determinations of the per cent of bromine in bromide of antimony, whose results are given beyond (p. 18), the maximum difference from the mean value 66.6651 was only 0.0045, and Professor Mallet, in his analyses of bromide of aluminum, has obtained with the same method a similar degree of accuracy.*

In conclusion, we would again express our obligations to Mr. G. M. Hyams, who has assisted us in the work of this investigation.

IV. Additional Experiments on the Atomic Weight of Antimony.

In our previous paper on this subject, we gave our reasons for the opinion, since fully confirmed, that the bromide of antimony is the

* Philosophical Transactions, Part III. 1880, 1022.

most suitable compound of this element, as yet known, for determining its atomic weight; and the results of fifteen analyses of five different preparations of the bromide were published, which gave for the atomic weight in question the mean value 120.00 with an extreme variation between 119.4 and 120.4 for all the fifteen analyses, and between 119.6 and 120.3 for the six determinations in which we placed most confidence. The antimonious bromide used in these determinations was purified first by fractional distillation, and secondly by crystallization from a solution in sulphide of carbon. In the crystallized product thus obtained, the bromine was determined gravimetrically as bromide of silver in the usual way. Although it seemed at the time that the results were as accordant as the analytical process would yield under the unfavorable conditions, which the presence of a large amount of tartaric acid in the solution of the bromide of antimony necessarily involved; yet it was obvious that the agreement was far from that which was desirable in the determination of an atomic weight, and our chief confidence in the accuracy of the mean value — independently of its remarkable agreement with previous results — was based on the fact that the known sources of error tended to balance each other. Hence our conclusions were stated with great caution, and the hope was expressed that, after a more thorough investigation of the subject, we might be able "to return to the problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible."

In our previous paper, we described a simple apparatus which we devised for subliming iodide of antimony; and in a note to the paper we stated that we were applying the same process to the preparation of bromide of antimony, and that it promised excellent results. Our expectations in this respect have been fully realized, and the product leaves nothing to be desired, either as regards the beauty or the constancy of the preparation. The fine acicular crystals are perfectly colorless, and have a most brilliant silky lustre. With ordinary precautions, they can be kept indefinitely without change, and it is easy therefore to determine the weight of the material analyzed to the tenth of a milligramme.

The material used in the following determinations was first prepared as described in our previous paper. It was then repeatedly distilled from a small glass retort rejecting at each distillation the first and the last portion. Lastly, it was twice sublimed in a slow current of absolutely dry carbonic dioxide. As it was only possible to sublime a

few grammes at a time in the apparatus we used, and as the several products were not mixed, each of the portions analyzed was the yield of a separate sublimation, and the agreement of the results is therefore in itself a proof of the constancy of the preparation. In the first set of analyses, the bromine was determined gravimetrically by precipitation with nitrate of silver, as before described. The bromide of antimony was first dissolved in a concentrated solution of tartaric acid, using about five grammes of the crystallized acid to a gramme of the bromide, and the solution was then diluted with from 250 to 500 cubic centimetres of water. To this solution was slowly added, under constant agitation, a solution of nitrate of silver in slight excess of the amount required for complete precipitation. The amount of crystallized nitrate of silver required was always carefully weighed out, allowing one decigramme in excess of theory for every litre of the solution of bromide of antimony made as above described. The nitrate of silver was then dissolved in a considerable volume of water, and the bromide of silver was precipitated from a cold solution, care being taken to prevent the formation of lumps which invariably result if the solutions are warm or concentrated, and which greatly interfere with the washing of the precipitate. The precipitate was washed by decantation five times, pouring on in each case a volume of lukewarm distilled water equal to that of the original solution, and after the precipitate had settled, drawing off the wash-water with the inverse filter (see these Proceedings, Vol. XII. page 124.) Lastly, the precipitate was transferred to a porcelain crucible, and dried at from 120° to 130°.

The bromide of silver weighed was always tested, sometimes by dissolving the material in strong aqua ammonia, and at other times by heating it to the melting point. Had there been the least occlusion of silver emetic, or any other possible product, there would have been an insoluble residue or a loss of weight; and, since the bromide of silver always gave a perfectly clear solution, and the loss of weight on melting never exceeded a few tenths of a milligramme, we were assured that our product was perfectly pure.

Of the five determinations whose results are given below, the first three were made under my direction by Mr. G. De N. Hough; the last two were made with my own hands.

Analyses of Antimonious Bromide.

Determination of Bromine.

No.	Wt. of $SbBr_3$ taken in grammes.	Wt. of AgBr obtained.	Per cent of Br. Br = 80 Ag = 108.	Diff. from mean.	Value of Sb.	Diff. from mean.
1.	4.1767	6.5420	66.652	— 0.016	120.08	+ 0.08
2.	2.0250	3.1734	66.685	+ 0.007	119.90	— 0.10
3.	1.9999	3.1340	66.680	+ 0.012	119.93	— 0.07
4.	3.6985	5.7946	66.669	0.001	119.99	— 0.01
5.	2.8959	4.5361	66.653	0.015	120.08	+ 0.08
	Mean value		66.6679		119.996	
	Theory Sb. 120 requires		66.667			

The mean value of the percentage of bromine deduced from the fifteen analyses previously made (see these Proceedings, Vol. XII., page 54) was 66.666, which differs only by an inappreciable quantity from the mean of the above results. At the same time the results are much sharper, the maximum difference from the mean value having been reduced to less than one fifth of the previous amount, and to only 0.00025 of the quantity estimated, giving us with certainty the atomic weight of antimony within one one-thousandth of its value. It must be remembered, moreover, that, although these last results were obtained with the same compound as before, the material was prepared in a wholly different way. The material first used was purified by repeated crystallization from sulphide of carbon, — that last used by repeated fractional distillation and sublimation.

Hoping to reduce the limit of error to a still greater degree, we * were led to devise a volumetric method of testing the atomic weight of antimony, which, while it had all the advantages of the gravimetric method previously employed, is free from its sources of error. The method has also this great advantage, that it brings the question of the atomic weight of antimony down to a definite issue.

If the atomic weight of antimony were 122.00, it would require 1.7900 grammes of pure silver to precipitate the bromine from a solution of 2.0000 grammes of antimony bromide, while if the atomic weight of antimony were 120.00, it would require 1.8000 grammes of

* Since publishing our "preliminary notice," our attention has been called to the fact that a similar process was used by Professor J. W. Mallet of the University of Virginia in his investigation of the atomic weight of lithium, as it has since been used by him in his admirable work on the atomic weight of aluminum.

silver. Now it is easy to estimate volumetrically $\frac{1}{100}$ of this difference with certainty. We therefore prepared with great care a button of *pure** metallic silver, which we annealed, and rolled out to a thin ribbon. We then weighed out from two to four grammes of bromide of antimony, prepared by sublimation as described above, and dissolved this salt in an aqueous solution of tartaric acid, which we then transferred to a litre flask, and diluted to about 500 cubic centimetres. We next very accurately weighed out a quantity of silver slightly less than that which calculation showed was required for complete precipitation. This silver was dissolved in nitric acid, and the solution having been evaporated to dryness over a water bath, the silver salt was washed into the flask containing the bromide of antimony. As soon as the supernatant liquid had cleared, the small additional amount of a normal silver solution required to produce complete precipitation was run in from a burette, and measured with the usual precautions. We used no extraneous indicator, because it was important not to introduce any possibly new disturbing element into the experiment, and in the titration of bromine with silver, the normal and familiar phenomena, which mark the close of the process, furnish a very sharp indication. The details of one of the determinations were as follows: —

The weight of the bromide of antimony used amounted to 2.5032 grammes. To precipitate the bromine from the solution of this material, 2.2404 grammes of silver would be required if $Sb = 122.00$, and 2.2529

* A quantity of silver which had been reduced from chloride and bromide of silver, obtained as a product of previous analytical processes, was dissolved in nitric acid, and precipitated as chloride by hydrochloric acid. The precipitate was first boiled in aqua regia, and then thoroughly washed, after which the chloride was reduced by boiling with caustic soda and inverted sugar, and the precipitate, again washed, having been transferred to a porcelain crucible and dried, was heated to a low red heat in a muffle until the grains were sintered together. The sintered mass was melted on a block of prepared coke before a gas blow-pipe, and while cooling was covered with a reducing flame in order to prevent the occlusion of oxygen gas. The metallic button was next rolled out into a ribbon between steel rollers; and, after the ribbon had been annealed in a muffle, the surface was etched with dilute nitric acid, and afterwards scoured with sand. The metal thus prepared was preserved under distilled water. The oxygen occluded by the metal thus prepared must have been, if any, exceedingly small in amount; but, even allowing the average quantity found by Dumas in metal which had been melted in the air under ordinary circumstances, we calculated that this amount would only affect the third decimal place in the atomic weight of antimony; and it seemed therefore unnecessary to take so inappreciable an effect into consideration. Moreover, the great purity of our material was subsequently made evident.

if Sb = 120.00. We weighed out, with as much accuracy as if we were adjusting a weight, the smaller of these two quantities of metallic silver, and after dissolving the pure metal in pure nitric acid, evaporating the solution to dryness, and redissolving in water, we gradually added the whole of this silver solution to the litre flask containing the solution of bromide of antimony, in the manner described above. It was then found that 12$\frac{4}{10}$ cubic centimetres of a standard silver solution (one gramme of silver to the litre) were required to complete the precipitation. It will be seen that the weights of the bromide of antimony and silver used could be thus determined with the most absolute precision, and we have the greatest confidence in these values to the $\frac{1}{10}$ of a milligramme. Moreover, it will be noticed that the volumetric method is only used to estimate the difference in the atomic weight which has been in question, and that, if the method were only accurate to the $\frac{1}{10}$ of the quantity to be measured, it would give us the value of the atomic weight within $\frac{2}{10}$ of a unit, while if, as we had reason to believe, the process was accurate within one per cent, it would fix the atomic weight within $\frac{2}{100}$ of a unit.

By the method just described, the following results were obtained. The letters *a* and *b* indicate different preparations: —

	Wt. of $SbBr_3$ taken.	Total Wt. of Ag used.	Per cent of Br Ag = 108 Br = 80.	Corresponding value of Sb.
a 1.	2.5032	2.2528	66.6643	120.01
a 2.	2.0567	1.8509	66.6620	120.02
a 3.	2.6512	2.3860	66.6644	120.01
b 4.	3.3053	2.9749	66.6696	119.98
b 5.	2.7495	2.4745	66.6653	120.01
	Mean value,		66.6651	120.01
	Theory Sb. 120 requires		66.6666	
	" Sb. 122 "		66.2983	

The extreme variation from the mean in these determinations is less than one ten-thousandth of the quantity directly estimated, and corresponds to less than two ten-thousandths of the total value in the atomic weight of antimony. We have thus reached the extreme limit of accuracy with determinations on this scale. By using very much larger amounts of material, it is possible that we might still further diminish the limits of experimental error; but when we consider the further causes of error incident to handling so large an amount of

material, it seems doubtful whether any advantage would really be gained. At all events such determinations would require an expenditure of labor and skill which is not demanded in the present condition of chemistry.

While making the first three volumetric determinations, it became obvious that the mode of experimenting was highly favorable to the accurate estimation of the amount of bromide of silver formed; and, were we to repeat this investigation, we should adopt the same mode of precipitating bromine in all cases. The rotatory motion given to the liquid mass in the stoppered flask in order to hasten the "clearing up," after each fresh addition of the silver solution, tends very greatly to granulate and thoroughly wash the precipitate. In the last two determinations, therefore, we collected and weighed the bromide of silver formed, and this weight gave us a most important control over the whole work. In the previous work we assume that the ratio of $Ag : Br = 108 : 80$, and find that on this assumption $Br : Sb = 80 : 120$. But if we both determine the amount of silver required to precipitate a given weight of antimonious bromide, and also at the same time the weight of argentic bromide formed, it is obvious that we fix at once the ratio of three atomic weights ($Ag : Br : Sb$) independently of any assumption whatsoever. This, so far as we know, is a new feature in investigations of this kind, and evidently vastly diminishes the possibilities of error, and enhances the value of the result. We give in full the two determinations which were made in this way:—

No. 1.

Weight of tube and $SbBr_3$	22.2225	grammes.
" after transfer to flask	18.9172	"
" of $SbBr_3$ taken	3.3053	"
" of silver taken	2.9749	"
Weight of crucible and filter	44.3729	"
" " " with AgBr dried at 150° . .	49.5512	"
" " " after again heating	49.5512	"
" " AgBr dried at 150°	5.1783	"
Weight of crucible and AgBr after removing small filter with adhering particles . . .	49.5008	"
Weight after heating AgBr. to incipient fusion .	49.5007	"
Reduced weight of AgBr	5.1782	"
Per cent of bromine	66.665	"
Atomic weight of antimony	120.01	"

No. 2.

Weight of tube and $SbBr_3$	32.4979	grammes.
" after transfer to flask	29.7484	"
" of $SbBr_3$ taken	2.7495	"
" of silver taken	2.4745	"
" of crucible and filter	44.3732	"
" " " with AgBr dried at 150° . .	48.6810	"
" " " after again heating	48.6810	"
" " AgBr dried at 150°	4.3078	"
Weight of crucible and AgBr after removing small filter with adhering particles . . .	48.5524	"
Weight after heating AgBr to incipient fusion .	48.5522	"
Reduced weight of AgBr	4.3076	"
Per cent of bromine	66.667	"
Atomic weight of antimony	120.00	"

Bringing now these results together, we have two additional gravimetric determinations of the atomic weight of antimony.

Weight of $SbBr_3$ taken.	Weight of AgBr determined.	Per cent of Bromine Ag = 108 Br = 80.	Corresponding value of Sb.
b 6. 3.3053	5.1782	66.665	120.01
b 7. 2.7495	4.3076	66.667	120.00
Mean value,		66.666	120.00

It is now obvious that these gravimetric determinations, taken in connection with the corresponding volumetric results, give us the most conclusive evidence of the purity, both of the metallic silver used, and also of the bromine in the bromide of antimony, which is the basis of this atomic weight investigation. By comparing *b* 6 and *b* 7 with *b* 4 and *b* 5 respectively, we obtain the following data: —

1. 2.9749 grammes of silver gave 5.1782 grammes bromide of silver.
2. 2.4745 " " " 4.3076 " " "

Hence it follows that, as shown by these experiments, the proportions of the silver to the bromine were respectively: —

	1. 108.00	silver to	79.99 bromine.
	2. 108.00	" "	80.01 "
Mean value	108.00	" "	80.00 "

This is the ratio of the atomic weight of silver to that of bromine, and corresponds to the second decimal place with the determinations of Stas as well as with those of Dumas.

We have now furnished as evidence of the atomic weight of antimony, —

1. The mean of fifteen analyses of bromide of antimony purified by crystallization from sulphide of carbon, with an extreme variation between 119.4 and 120.4 for all the fifteen analyses.

2. The mean of five analyses of bromide of antimony purified by distillation and sublimation, with an extreme variation between 119.90 and 120.08.

3. The mean of five volumetric analyses of bromide of antimony, also purified by distillation and sublimation, with an extreme variation between 119.98 and 120.02.

4. Two gravimetric determinations of the bromine in two of the portions of bromide of antimony used in the volumetric analyses, but still essentially distinct determinations, which gave almost identical results.

Bringing these several means together as of equal value, we have :—

	Per cent of Br.	Value of Sb.
1. Mean of fifteen determinations	66.666	120.00
2. " five "	66.668	119.99
3. " five "	66.665	120.01
4. " two "	66.666	120.00
Final mean value,	66.666 +	120.00

Furthermore, we have shown by the last two determinations, that the ratio of the atomic weight of the silver to that of the bromine, used in our experiments, was 108.00 to 80.00, and hence that the ratio of the atomic weights of bromine silver and antimony must be

$$Ag : Br : Sb = 108.00 : 80.00 : 120.00,$$

with a probable error not exceeding 0.01 in any case. Of course our experiments only serve to fix the ratio between these three quantities, and any considerations which may lead chemists to change the value of one of the quantities must affect the other two in the same proportion. If with Stas we take $Ag = 107.66$, then $Br = 79.75$, and $Sb = 119.63$; and in this connection the fact should be recalled that the ratio of Ag to Br, according to Stas, is essentially identical with that given above, and the same as that found both by Dumas and by Ma-

rignac. Of all the ratios between the atomic weights, it is the one in regard to which there is the greatest certainty; and it is with this very well established relation that we have connected the atomic weight of antimony.

Entirely in harmony with the above results are our experiments on the synthesis of sulphide of antimony, in which we found as a mean of thirteen experiments $Sb = 119.94$ when $S = 32$; and the same is equally true of our analyses of iodide of antimony, which gave as a mean of seven determinations $Sb = 119.98$ when $I = 127.00$. But although these results formed important stages in our investigation, they now add but little to the evidence of the far more accordant results since obtained. When compared with these later results they show, however, to what a great extent error may be eliminated by the repetitions of an imperfect process.

Lastly the anomaly which the analysis of antimonious chloride first presented has been explained by finding, first, that the material employed contained a constant amount of oxichloride; and, secondly, that the water used in washing the precipitate exerted a definite solvent action on the chloride of silver estimated.

Having thus solved the problem we undertook as far as is at present practicable, we must now take leave of the subject, regretting only that our investigation should have been the occasion of any controversy. In addition to the recognition we made in our previous paper, we would here express our obligations to Mr. G. De N. Hough and Mr. G. M. Hyams, who have greatly aided us in the experimental work during the latter part of this investigation.

V. — The Boiling Point of Iodide of Antimony, and a New Form of Air Thermometer.

In continuation of our investigations on the Haloid Compounds of Antimony, the boiling point of antimonious iodide has been determined by Mr. W. Z. Bennett, at the time a student in this laboratory. The observations were made with Regnault's air thermometer, but it was found possible to simplify very greatly the details of the process without seriously impairing the accuracy of the result. For temperatures above the range of a mercury thermometer's measurements, accurate to one degree centigrade, are all that the uncertain conditions of most problems permit, and all, therefore, that the circumstances demand. As used by Regnault, the air thermometer is capable of measuring such temperatures accurately to the one tenth of a degree,

and by multiplying observations possibly to the one hundredth of a degree. In his admirable investigation of the boiling point of sulphur at different temperatures, the observations of temperature are undoubtedly accurate to this extent; but Regnault's own discussion of these observations plainly indicates that there must have been unknown or accidental causes influencing his experiments, which render the results uncertain to at least one degree; and the boiling point of sulphur is still in doubt to this extent. It should be added, however that there are only a very few boiling points which are known more accurately; for, even when within the range of a mercury thermometer, an observation of a boiling point, to be accurate to a tenth of a centigrade degree, requires an attention to circumstances which is seldom bestowed on such observations.

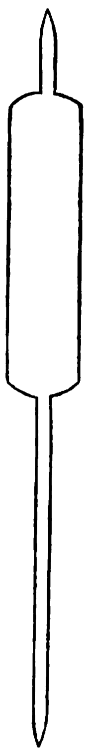


FIG. 1.

The glass thermometer-bulb used in our experiments is represented in the accompanying figure (Fig. 1) of one half the actual size in its linear dimensions. The longer stem was made of thermometer tube, and a shorter stem was added to the opposite end of the bulb in order to facilitate the cleaning, drying, filling, or emptying of the interior, all of which was easily accomplished by the aid of a Bunsen pump. The shorter stem was of course sealed after the bulb had been dried and made ready for use, and before it was immersed in the medium whose temperature was to be measured. After an equilibrium had been established at this unknown temperature, T'°, the protruding end of the longer stem was sealed, and at the same time the height of the barometer, H, was noted. The bulb was then taken to a room of uniform temperature provided in the laboratory for gas analysis, and, after being mounted on a convenient support, the end of the stem was broken off under mercury, and the apparatus left to itself for a time to secure a perfect equilibrium of temperature. This temperature, T°, was then observed, by means of a standard thermometer hanging near the bulb; also the height, h, to which the mercury had risen in the bulb, was measured by a cathetometer; and in addition the height, H', of a barometer (hanging in the same room) was noted. Closing now the open stem with the finger, the bulb was quickly inverted and the containing mercury drawn out into a tarred vessel and weighed (nipping off the extreme end of the shorter stem for the purpose). This gave the weight, w. Lastly, the bulb and stem having

been completely filled with mercury by suction, the weight W, corresponding to their total capacity was obtained in a similar way. The required temperature could now be calculated by means of the well-known law of Charles: —

$$T^{\circ\prime} + 273^{\circ}.2 = (T^{\circ}. + 273^{\circ}.2)\ \frac{W}{W - w} \cdot \frac{H}{H' - h}\,[1 + (T^{\circ} - T^{\circ\prime})\,k]$$

It will be noted that as the mercury columns, including the heights of the barometer, were all measured at the same constant temperature; and, as we are dealing with relative values only, no reductions are necessary. Moreover, an error of one tenth of a millimetre in the value of $\frac{H}{H' - h}$ would make, in determining the boiling point of sulphur (448°), a difference of only one eighth of a degree, so that measurements of these heights are sufficiently close, if accurate, to one half a millimetre, and might even be made with a common rule. The most uncertain element in the formula is the expansion of glass; but if the bulbs are made of flint glass (lead glass) tubing, such as is used in this neighborhood for ornamental ware, the mean coefficient of expansion will vary very little from 0.000025, if the temperature does not exceed that at which the glass begins to soften. The rate of expansion of flint glass is not only less than that of crown, but it is also more constant, and increases very slowly with the temperature. Flint glass is therefore better adapted for the use we are describing. The expansion of the glass used in our experiments was carefully determined, and found to have the value given above, within two or three tenths of a unit in the last place. A difference of one unit in this place would make a difference of one third of a degree in the boiling point of sulphur.

In order to test the accuracy of this method, Mr. Bennett made four determinations of the boiling point of sulphur under different barometric conditions, which in the following table are compared with the results of Regnault, reduced to the corresponding pressures: —

Barometer. Height at 0°.	Boiling Point of Sulphur. Bennett.	Regnault.	Diff.
758.8	447.4	447.3	+ 0.1
763.9	448.2	447.7	+ 0.5
769.6	448.2	448.1	+ 0.1
776.7	448.2	448.7	— 0.5

Regnault made eight observations on the maximum tension of sulphur vapor at temperatures varying from 387°.64 to 554°.03, and from a discussion of these deduced the constants of an exponential formula, by which he calculated a table of maximum tensions for every ten degrees between the extreme limits, and also plotted a corresponding curve. It so happens, however, that the only two observations within the range of ordinary atmospheric pressure fall outside, and on the same side, of this assumed curve. These observations are the ones usually taken as indicating the boiling point of sulphur; and Victor Meyer, in one of his methods of determining the density of the vapors of substances which have a high boiling point, assumes a value for the boiling point of sulphur (at the mean atmospheric pressure at Zurich), which he obtains by simple interpolation from the two observations just referred to.* In like manner we have calculated the above values corresponding to the pressures at which Mr. Bennett's results were obtained on the basis of the same two observations; but, instead of simply interpolating by the first differences, we have assumed that the variation between the two observed values would follow the law indicated by the general curve, which Regnault gives as the best expression for all his observations. But according as we take the two observations, or the whole, we obtain values for the boiling point of sulphur differing by more than a degree; and hence, as we have already said, there is still an uncertainty in regard to the boiling point to this extent. As is evident, Mr. Bennett's observations confirm very closely the interpretation of Regnault's results, adopted by both Victor Meyer and by ourselves.

After the accuracy of our method had been thus placed beyond doubt within the limits required, Mr. Bennett made three determinations of the boiling point of antimonious iodide, with the following results: —

Barometer. Height at 0°.	Boiling Point of SbI_3.
758.1 millimetres.	400°.4
758.4 "	400°.9
759.3 "	400°.9

Probably only a small part of the difference between these observations depends on the variations of pressure. We only regard the method as accurate to whole degrees, and 401° is evidently the boiling

* Fresenius's Zeitschrift, xvi. 482.

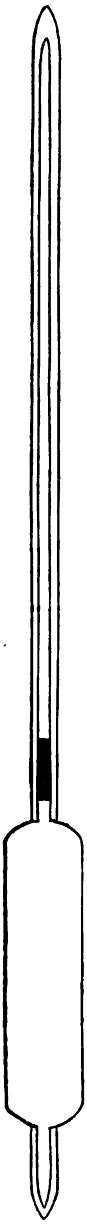


FIG. 2.

point of antimonious iodide at the normal pressure of the air within half a degree on either side.

The method we have here described we can most confidently recommend as a most efficient and accurate means of determining high temperatures in chemical laboratories. It requires no expensive apparatus, and no more delicate manipulation than most processes of gas analysis. Indeed, this method is most readily associated with Bunsen's methods of gas analysis; and, in a laboratory provided with a room fitted for that work, the observation of temperature we have described can be made in a very short time.

In connection with these experiments, we were led to devise a very simple and inexpensive form of differential air thermometer, that can be used almost as readily as a mercury thermometer, and which will measure either high or low temperatures with all the accuracy that is usually required. The instrument is represented by Fig. 2 of one half its linear dimensions. The long stem is made of "barometer tubing," a little over a millimetre in diameter, and by careful calibration is arbitrarily divided into parts of equal capacity, making, we will say, two hundred divisions on the length of the stem. While the instrument is still open at both ends it is easy to determine, first, the weight of mercury which fills the bulb up to the first division of the stem; and secondly, the weight of a column of mercury covering an observed number of divisions of the stem. These constants being known, and the interior of the instrument having been most carefully dried, for which the two openings offer great facilities, a short column of very pure mercury is introduced, and brought into the position represented in the figure. The two ends are now hermetically closed with a blow-pipe, and the instrument is made. It can be used either in a vertical or horizontal position, although the zero point of the scale is slightly different in the two cases, owing to the weight of the short mercury column. Of course this column remains immovable so long as the temperature of the two ends remains the same; but when the bulb is heated, the column, which we will call the index, moves up the stem, which becomes a closed monometer. If the instrument is to be used for measuring low temperatures, the index should be placed about one third way up

the stem before closing the open ends. The theory of the instrument is the same in either case, but in our description we will assume that the index has been set for measuring high temperatures, as shown in our figure.

As the instrument is a differential thermometer, its accuracy depends on keeping the stem at a *constant* and *known* temperature; and from this constant temperature the observed temperatures are deduced. When the thermometer is held in a horizontal position, and the stem can be protected from the neighboring sources of heat, it is sufficient to place a standard mercury thermometer at the side of the stem; but it is always better, and generally necessary, when the stem is in a vertical position over the source of heat, to surround the stem with a jacket, through which circulates a stream of water of known temperature. This temperature we will call the temperature of reference, and represent by $T°$. In order now to determine the value in centigrade degrees of the division of the instrument, we place it in the position in which we propose to use it, and when the two ends are at the same temperature, we observe the position of the two ends of the index on the graduate scale. We can now easily find from the weights obtained before closing the instrument, first the weight of mercury which would fill the bulb and stem up to the index, which we call W; and, secondly, the small weight of mercury which would fill one division of the stem which we will call w. We have also, by observation, the number of division on the stem above the index. This number, which we count from the closed end of the stem, we will represent by N.

Assume now that the bulb and stem up to the index is immersed in a medium which has the temperature, T'. The index moves, and in its new position let N' represent the number of division on the stem above the index. We can now easily deduce the following values: —

$\frac{N}{N'}$ = the ratio of the tension of the confined air at $T'°$ and $T°$.

$N - N'$ = the number of division through which the index moved.

$\frac{W + (N - N')\,w}{W}$ = the ratio of the volumes of the air in the bulb at $T°$ and $T'°$, independent of the expansion of the glass.

$\frac{W + (N - N')\,w}{W}\,(1 + [T - T']\,k)$ = same ratio, allowing for expansion of glass.

Then, as we can easily deduce from the laws of Mariotte and Charles: —

$$T'^{\circ} + 273 = \frac{N}{N'}(T^{\circ} + 273)\frac{W + (N - N')\,w}{W}(1 + [T^{\circ} - T'^{\circ}]\,k)$$

With this formula, it is now easy to compute the values for each division of our arbitrary scale. We cannot, however, depend absolutely on the result, as there are several causes which will differ with each instrument, and of which we can take no account. It is therefore best to observe, with the instrument, two or three well-established boiling points, which will give us fixed points by which we can correct the table, and we shall then have an instrument whose precision is fully equal to that of a mercury thermometer.

It is, of course, very desirable that the temperature of reference T° should be always the same and as invariable as possible. This is best accomplished, as above suggested, by maintaining a circulation of water through a glass jacket surrounding the stem of the instrument and enclosing also a small mercury thermometer, which is best tied to the stem. By selecting the temperature of reference a little higher than the highest temperature of the water supplied by the laboratory hydrants, it is easy to maintain the required temperature within a degree by regulating the flow. The instrument may then be adjusted to the tubulature of a retort and used in fractional distillations.

VI. Revision of the Atomic Weight of Cadmium.

By Oliver W. Huntington, *of the Senior Class.*

The method adopted by Professor Cooke for verifying the value of the atomic weight of antimony, described in this volume (page 16), proved to be so definite and conclusive, that it seemed desirable to apply it in all other cases to which it was suited, in order not only to verify the received values of the atomic weights, but also to test more fully the hypothesis of Prout, an hypothesis to which recent investigation and speculations have given renewed interest.*

The method of Professor Cooke is applicable to all those elements of which a pure, stable, well-defined, and soluble bromide can be pre-

* See Revision of the Atomic Weight of Aluminum, by J. W. Mallet, Philosophical Transactions, part iii. 1880: also various papers by J. Norman Lockyer on the disassociation of the chemical elements in "Nature" and in the Proceedings of Royal Society; also Cooke's Chemical Philosophy, revised edition, page 272.

pared. It consists in determining in one series of analyses the bromine of the compound as bromide of silver by the usual gravimetric method with the precautions already described (page 19); and in another series of experiments, or in the same analyses, when practicable, determining the amount of silver required to precipitate the bromine. We thus obtain not only the relation of the atomic weight sought both to that of bromine and to that of silver; but also the relation between the atomic weight of bromine and that of silver; and since all experimenters agree on this last ratio to within one ten-thousandth of its value it is evident that the comparison of the two series of results gives a sharp control of the accuracy of the work.

Professor Cooke assigned to me the atomic weight of cadmium as my portion of the work he had planned on the revision of the atomic weights, and this investigation was made with his aid and under his immediate direction. Bromide of cadmium fulfils all the conditions which the new method requires; and, since the accepted value of the atomic weight of cadmium is a whole number, it seemed probable that a revision of this value by a more exact process would bring additional evidence in support of the hypothesis of Prout.

Having found that bromide of cadmium could not readily be purified by repeated crystallizations on account of its very great solubility in water, we sought to obtain a pure compound by preparing pure carbonate of cadmium on the one hand and pure hydrobromic acid on the other.

To prepare pure carbonate of cadmium the commercial metal was first dissolved in pure hydrochloric acid. From this solution, still strongly acid, sulphide of cadmium was precipitated by sulphide of hydrogen, and the precipitate thoroughly washed with hot distilled water. The sulphide having been redissolved in hydrochloric acid, and the resulting sulphide of hydrogen expelled by boiling, the cadmium was next precipitated as carbonate by carbonate of ammonia, and the precipitate digested with a large excess of this reagent. The white carbonate thus obtained was thoroughly washed and redissolved in hydrochloric acid; and the same series of precipitations repeated. Lastly, in order to remove any possible trace of adhering chloride, the carbonate of cadmium which had thus been twice precipitated by carbonate of ammonia, and twice digested with a large excess of this reagent, was dissolved in pure hydrobromic acid, and a third time precipitated and digested with pure carbonate of ammonia.

The hydrobromic acid used in this investigation was made by the process described by Dr. Edward R. Squibb, of Brooklyn, in the

Transactions of the Medical Society of the State of New York.* In order to purify the acid, it was repeatedly redistilled with a small amount of a concentrated solution of bromide of potassium, rejecting each time the distillate until the boiling point rose to 128°; when, as is well known, an acid containing about 47 per cent of HBr distils unchanged. The acid thus obtained was as colorless as water.

Meanwhile, in order to test the purity of the hydrobromic acid and also as a basis for the rest of our investigation, we prepared a quantity of pure silver by the method already fully described in a previous part of this volume (page 17); and with the pure silver thus prepared the following two sets of determinations were made.

For the first set, weighed amounts of silver were dissolved in very carefully purified nitric acid, using only a very slight excess of this solvent in any case. We prepared for the purpose a dilute acid by mixing one part of acid, having Sp. Gr. 1.355, with four parts of water and of this weak acid 5. 3 c. m.^{3} were required for each gramme of silver. We were thus able to estimate the amount necessary for each analysis, and we used generally one half a cubic centimetre in excess.

The silver having been perfectly dissolved, and the solution diluted with water to from two hundred to five hundred cubic centimetres, according to the amount of silver used, we gradually and cautiously precipitated bromide of silver by adding pure hydrobromic acid, prepared as just described, but greatly diluted until the acid was very slightly in excess. For the method of washing and collecting this

* "The formula and process for making an acid of this strength are as follows: —

Take of Potassium Bromide	Six parts.
Sulphuric Acid, Sp. Gr. at 15°.6 C. 1.838, at 25 ° C. 1.828 . . .	Seven parts.
Water	Nine parts.

"Add to the sulphuric acid one part of the water and cool the mixture. Then dissolve the potassium bromide in six parts of the water by means of heat, supplying the loss of water by evaporation during the heating. Pour the diluted sulphuric acid slowly into the hot solution with constant stirring, and set the mixture aside for twenty-four hours, that the sulphate of potassium may crystallize. Pour off the liquid into a retort, break up the crystalline mass, transfer it to a funnel, and, having drained the crystals, drop slowly upon them two parts of the water so as to displace and wash out the acid liquid. Add the liquid, thus drained off and washed out, to that in the retort, and distil the whole nearly to dryness, or until nothing further distils off by moderate heating. The distillate will weigh about ten parts and should contain about thirty-seven per cent of hydrobromic acid."

precipitate, we may refer to Vol. XII. page 124, of these Proceedings. The results were as follows: —

	Weight of Silver.	Weight of Bromide of Silver.	Per Cent of Silver.
1.	1.4852 grammes.	2.5855 grammes.	57.444
2.	1.4080 "	2.4510 "	57.446
3.	1.4449 "	2.5150 "	57.451
		Mean Value	57.447

For the second set of experiments bromide of silver precipitated, washed, and dried as described (loc. cit.), was melted in a platinum crucible, and then reduced by a voltaic battery under dilute sulphuric acid. This process was devised and perfected by Mr. L. P. Kinnicutt, Assistant in this Laboratory, who had the great kindness to conduct the reduction in the following determinations.

	Weight of Bromide of Silver.	Weight of Silver.	Per Cent of Silver.
1.	4.1450 grammes.	2.3817 grammes.	57.444
2.	1.8172 "	1.0437 "	57.434
3.	4.9601 "	2.8497 "	57.449
		Mean Value	57.442

These results show conclusively the great accuracy of Mr. Kinnicutt's process, which he will describe in detail in another place. The mean of the two sets of results gives for the per cent of silver 57.445, the theoretical per cent ($Ag = 108$ and $Br = 80$) being 57.446. If we throw out No. 2 of second series, which is obviously less trustworthy than the other two determinations of the same series, on account of the comparatively small amount of material used, the mean of the remaining five determinations corresponds absolutely to theory, and the total result, therefore, leaves no doubt whatever as to the absolute purity of the materials employed.

Bromide of cadmium was now prepared by dissolving pure carbonate of cadmium in pure hydrobromic acid, and subliming the product previously dried at 200° in a current of pure and perfectly dry carbonic dioxide gas. The carbonic dioxide was prepared by mixing bicarbonate of soda and sulphuric acid with a large volume of water in a strong generator, and drawing off the gas under pressure through appropriate washers and driers; and the apparatus used for subliming the bromide of cadmium was similar to that described in these Proceed-

ings, Vol. XIII. page 57, using however a porcelain tube heated by a gas furnace in place of a tube of glass. The bromide of cadmium when thus sublimed crystallizes in pearly scales around the open mouth of the tube.

Prepared as we have described, anhydrous bromide of cadmium is a splendid preparation. The precise form of the highly lustrous crystals could not be distinguished, but the scales are tubular crystals having a single optical axis normal to the extended face of the scales and having a high negative double refracting power. Although so soluble, the crystals are not sensibly hygroscopic, and can be weighed on an open watch-glass without the slightest variation of weight during the process. They dissolve at once in water without leaving a trace of residue.

The following determinations were all made with the material we have described, and since only a few grammes could be sublimed at a time, the separate analyses were made with the products of nearly as many sublimations. Some of the material was sublimed twice, and the constancy of the composition under these circumstances is the best proof possible of the definiteness of the compound. The results of the analyses may be classed under two heads.

In one series of determinations, the bromide of antimony, whose weight had been accurately determined, having been dissolved in pure water in a stoppered flask, a little less than the calculated amount of silver required to precipitate the bromide was carefully weighed out and dissolved in a measured amount of weak nitric acid allowing as before described a slight excess. This solution properly diluted was then gradually added to the solution of bromide of cadmium under constant agitation in order to avoid the aggregation of the bromide of silver in lumps. The agitation was frequently renewed until the precipitate settled, and then a standard solution of silver (one gramme to the litre) was cautiously added until the precipitation was complete, and the last drops did not produce the faintest opalescence after standing. The precipitate was now washed by decantation five times successively, using each time a volume of cold distilled water equal to the volume of the original solution, and pouring off the water into a porcelain crucible, from which it was drawn by the reverse filter. Finally, the precipitate was washed into the crucible, and after drying at from 120° to 130° weighed with the small filter.

In a second series, the determinations were conducted in the same way as in the first, excepting that the chief attention was directed to determining the exact point of complete precipitation. In several cases, indicated by an asterisk, both the amount of silver required, and

the amount of argentic bromide formed were determined in the same experiment; but this was not always practicable.

FIRST SERIES.

	Weight of Bromide of Cadmium.	Weight of Bromide of Silver found.	Value of Cd when Ag = 108 and Br = 80
1.	1.5592 grammes.	2.1529 grammes.	112.32
2.*	3.7456 "	5.1724 "	112.28
3.	2.4267 "	3.3511 "	112.28
4.*	3.6645 "	5.0590 "	112.36
5.*	3.7679 "	5.2016 "	112.36
6.	2.7938 "	3.8583 "	112.27
7.*	1.9225 "	2.6552 "	112.26
8.	3.4473 "	4.7593 "	112.34
		Mean Value	112.31

SECOND SERIES.

	Weight of Bromide of Cadmium.	Weight of Silver required.	Value of Cd when Ag = 108 and Br = 80
1.*	3.7456 grammes.	2.9715 grammes.	112.27
2.	5.0270 "	3.9874 "	112.30
3.*	3.6645 "	2.9073 "	112.26
4.*	3.7679 "	2.9888 "	112.30
5.*	1.9225 "	1.5248 "	112.33
6.	2.9101 "	2.3079 "	112.35
7.	3.6510 "	2.8951 "	112.39
8.	3.9782 "	3.1551 "	112.35
		Mean Value	112.32

As can easily be calculated according to the mean of the first series of determinations, 1.0000 gramme of bromide of cadmium gives 1.3808 grammes of argentic bromide, and according to the mean of the second series 1.0000 gramme of bromide of cadmium requires for complete precipitation 0.7932 gramme of silver. Hence, as a mean of these experiments, 0.7932 gramme of silver yields 1.3808 grammes of argentic bromide and therefore corresponds to 0.5876 gramme of bromine. Moreover, since

$$0.7932 : 0.5876 = 108.000 : 80.006,$$

it follows with a very high degree of probability that

$$Ag : Br : Cd = 108.00 : 80.00 : 112.31,$$

within one ten-thousandth of the value of either quantity. It must of course be regarded as absolutely proved that, in the material analyzed, the proportion of bromine to the remainder of the mass, assumed to be pure cadmium, is as 2×80.00 to 112.31, but it is always conceivable that the material used contained some unknown impurity. In the present case, however, such an assumption is highly improbable; first, because such extreme care was taken in the preparation; secondly, because the products of the different sublimations were so constant in composition; and, thirdly, because the presence of any of the metals usually associated with cadmium would tend to lower and not to raise the apparent atomic weight. If any impurity is present, it would seem as if it must be some unknown element, and only on such a bare chance as this can the evidence be invalidated which the results of this investigation furnish against the hypothesis of Prout.

ON

AN APPARENT PERTURBATION

OF THE

LAW OF DEFINITE PROPORTIONS

OBSERVED IN THE COMPOUNDS OF

ZINC AND ANTIMONY.

BY JOSIAH P. COOKE, JR., CAMBRIDGE.

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ON AN APPARENT PERTURBATION, &c.

In a former paper in this Journal* I described two new compounds of zinc and antimony Sb Zn_3 and Sb Zn_2 which I named respectively, Stibiotrizincyle and Stibiobizincyle, because they resemble in their composition the metallic radicals of organic chemistry, and because the first decomposes water rapidly at 100° C. I there stated that crystals of Sb Zn_3 could be obtained containing a much larger amount of zinc than that required by the law of definite proportions, and that this change was not accompanied by any alteration of crystalline form. A similar variation of composition was afterwards observed in the crystals of Sb Zn_2, and it is the object of the present paper to describe the law of the variation in both cases and to explain its cause.

In the course of my investigations on this subject, crystallizations were made or attempted of alloys differing in composition by one half to five per cent., according to circumstances, from the alloy containing 95 per cent. of zinc to that containing 95 per cent. of antimony; but only two crystalline forms were observed, that of Sb Zn_3 and that of Sb Zn_2. Well defined crystals, like those described under Sb Zn_2 in the former paper,† were obtained from the alloys between 43 and 60 per cent. of zinc; and even in alloys of a higher zinc per-centage, crystals of the same form were still seen, although they were no longer well defined. In the alloys between 20 and 33 per cent. of zinc, well defined crystals, like those described under Sb Zn_3 in the same paper, were formed; and finally there separated from the alloys between 33 and 42 per cent. of zinc thin metallic plates, which evidently belonged to the same crystalline form. In making the alloys from 43 to 95 per cent. of zinc, the zinc was melted first,

* This Journal, vol. xviii, p. 284. † Ibid.

and when in fusion the antimony was added. As the melting point of antimony is much above that of zinc, the fluid zinc acted on the solid antimony as a solvent, dissolving the pure metal, but not the impurities, which rose to the surface forming a scum. This scum seemed to take with it some of the antimony and thus caused a loss, which, together with the impurity, was found by experiment to be about three per cent. of the antimony used. This resulted in raising the per-centage of zinc in the alloy at most about eight-tenths of one per cent. The alloys below 43 per cent. of zinc were made by melting the antimony first, and then adding zinc. By this method the loss of antimony was very greatly diminished, and, counting the impurity, was found to be only about one per cent. and a half of the antimony used. In preparing the alloys this loss was always allowed for, and the crystallizations were all made as nearly as possible under the same circumstances, so that any unexpected cause of error should affect all equally. The crystals formed in the alloys were all analyzed in my laboratory under my direction and immediate supervision, and the greater part of them by myself. The rest were by my assistants, Mr. F. H. Storer, Mr. C. W. Eliot, and Mr. C. S. Homer, to whose care and accuracy I take pleasure in bearing witness. Their work is in all respects as reliable as my own. The results are collected in the following table which will explain itself.

Analyses of the Crystals formed in the Alloys of Zinc and Antimony.

STIBIOTRIZINCYLE.						STIBIOBIZINCYLE.					
Composition of the Alloys by Synthesis.		Composition of the Crystals by Analysis.			Name of the Analyst.	Composition of the Alloys by Synthesis.		Composition of the Crystals by Analysis.			Name of the Analyst.
Per ct of Zn.	Per ct. of Sb.	Per ct. of Zn.	Per ct. of Sb.	Sum.		Per ct. of Zn.	Per ct. of Sb.	Per ct. of Zn.	Per ct. of Sb.	Sum.	
70·40	29 60	64 15	35·77	99·92	Cooke.	33·00	67 00	35·37	64·57	99·94	Cooke.
66 50	33·50	61·00	39·00	*100·00	Cooke.	do.	do.	35·40	64·60	†100·00	Cooke.
64·50	35 50	53 50	41·44	99·94	Cooke.	32 50	67·50	34·62	64 92	99·54	Storer
. .	. .	55·49	44·42	99·91	Homer.	do.	do.	34·61	65·39	†100·00	Eliot.
60·60	39·40	55·00	45·09	100·09	Homer.	31·50	68·50	33·95	66·09	100 04	Storer.
58·60	41·40	50·39	49·29	99·68	Eliot.	29 50	70·50	33·62	66 38	†100·00	Storer.
56·60	43·40	49·92	50·05	99·97	Eliot.	do.	do.	33 62	66·38	†100 00	Storer.
54·70	45·30	48·26	51·42	99·68	Storer.	27·50	72·50	33 85	65 81	99·66	Storer.
52·70	47·30	47·47	52·53	†100·00	Cooke.	26 50	73·50	32 08	67·60	99·68	Storer.
. .	. .	. .	. .	. .	. .	26·00	74·00	30·74	69·06	99·80	Cooke.
50·70	49·30	46·89	53·11	†100·00	Cooke.	25 50	74·50	30·43	69·51	99·94	Storer.
do.	do.	46 45	53 55	†100·00	Cooke.	25·00	75 00	29 88	70·20	100·08	Cooke.
48·70	51·30	48·66	51·34	†100·00	Eliot.	24·50	75 50	28·76	71·24	100·00	Cooke.
46·70	53·30	46·77	53·23	†100 00	Eliot.	23·50	76 50	27·93	71·85	99·78	Cooke.
44·80	55·20	44·26	55·73	†100·00	Eliot.	22 50	77·50	26·62	73·27	99 89	Storer.
43·80	56 20	44 04	55·96	†100·00	Cooke.	21·50	78·50	24·83	74·74	99·57	Cooke.
42·80	58·20	43·15	56·93	100 08	Cooke.	20·12	79·88	20·58	79·42	100·00	Cooke.
do.	do.	43·06	56 50	99·56	Cooke.						
do.	do.	42·83	57 24	100·07	Cooke.						

* In this analysis the antimony only was determined.
† In this analysis the zinc only was determined.

Curve of Variation in Composition.—In order to compare together the composition of the crystals and that of the alloy in which they form, I have resorted to the usual method of Analytical Geometry, and in the plate illustrating this paper, the lower horizontal line is the axis of abcissas, and the vertical line at the extreme left the axis of ordinates. The first has been divided into equal parts, which denote the per cents. of zinc in the crystals and the last into parts of the same size, which stand for the per cents. of zinc in the alloys. The zinc rather than the antimony determinations have been selected for comparison, as being generally more accurate, and as having been all made in exactly the same way. The points determined by analysis are indicated with dots, and the double line drawn through these dots is a curve, which represents the relation of the composition of the crystals to that of the alloy in which they form. In order to make clear the connection between the two, it will be well to discuss this curve, commencing with what may be termed the two centres of crystallization, the alloys of 42·8 and 31·5 per cents. of zinc, and examining the effect produced on the crystals by diminishing or increasing the amount of zinc in the alloy.

It has already been stated that the crystals of $Sb\ Zn_3$ are obtained in their greatest perfection from the alloy of 42·8 p. c. of zinc. They are then comparatively large, generally aggregated, and, as the three analyses cited in the former paper prove, have the same composition as the alloy. On increasing gradually the amount of zinc in the alloy up to 48·7, the crystals continued to have the composition of the alloy, and the only difference, which could be observed in their character, was, that they were smaller and more frequently isolated. Between these limits, the whole mass of the alloy exhibited a strong tendency to crystallize, and, by pouring it, as it cooled, from one vessel to another, it could be crystallized to the last drop. The portion *a*, *b*, of the curve is therefore a straight line equally inclined to the two axes. On increasing the amount of zinc in the alloy to 50·7 p. c., the amount of zinc found in the crystals was only 46·89 p. c., and above this it was uniformly less than it was in the alloy; but no closer relation between the two could be detected, owing undoubtedly to the unavoidable irregularity in the crystallizations of the alloys, which contained more than 50 p. c. of zinc. This arose from a peculiar pasty condition, which the fluid mass assumed, at the point of crystallization, apparently caused by the separation of the excess of zinc. Definite crystals however were obtained even from the alloy of 60 p. c. of zinc, which contained 55 p. c.; above this, the crystals became less and less abundant, and gradually faded out, although the alloy even of 86 p. c. of

zinc exhibited a radiated crystalline texture; and a trace of this structure could still be discovered even in the alloy containing only 4 p. c. of antimony. It might be supposed that on returning to the alloy of 42·8 p. c. of zinc, and increasing the amount of antimony we should obtain crystals containing an excess of antimony; but so far is this from being true that the slightest excess of antimony entirely changes the character of the crystallization. On crystallizing an alloy containing 41·8 p. c. of zinc not a trace of any prismatic crystals could be seen, but in their place there was found a confused mass of thin metallic scales, which, as will soon be shown, are imperfect crystals of $Sb\,Zn_2$. Thus it appears that although perfectly formed crystals of $Sb\,Zn_2$ can be obtained containing 55 p. c. of zinc they can not be made to take up the slightest excess of antimony.

In order to obtain crystals having the composition of $Sb\,Zn_2$, that is, containing 33·5 p. c. of zinc, it is necessary to crystallize an alloy at least as low as 31·5 p. c. of zinc. At this point large compound crystals are obtained corresponding to the large crystals of $Sb\,Zn_3$. On increasing the amount of zinc in the alloy up to 33 p. c., the proportion of zinc in the crystals appeared to increase in the same ratio, so that the curve of $Sb\,Zn_2$ is at this part a straight line parallel to the curve of $Sb\,Zn_3$. It should however be noticed that the extent of this line *k i* is so limited that a very small error in the analyses might change very considerably its direction. The crystals of $Sb\,Zn_2$ containing an excess of zinc, are smaller and more frequently isolated than those containing exactly two equivalents. A similar fact, it will be remembered, is true of the crystals of $Sb\,Zn_3$. At the alloy of 33 p. c. of zinc, the definite crystals of $Sb\,Zn_2$ begin to disappear and are succeeded by thin metallic scales, which, as the two following facts will prove, are imperfect crystals of the same crystalline form. First, the scales from the alloy of 33 p. c. are frequently found having a definite crystal as a nucleus, when it is evident that their surfaces are extensions of the basal plane O of fig. 2 of the former memoir. Secondly, the scales twin together like the large tabular crystals of $Sb\,Zn_2$, forming a cellular structure, and the angle between two scales thus united, measured with an application goniometer approximately 115° 30′, and was therefore equal to the basal angle of the definite crystals. These scales continue up to the alloy of 41·8 p. c. of zinc, becoming however constantly less abundant and less distinct. Several specimens of them were analyzed, but no regularity in their composition could be detected except that they all contained a very much larger amount of zinc than the alloys in which they formed. This irregularity and the imperfection in the crystallization seem to be caused by the interference of $Sb\,Zn_3$, that is, by a tendency to form $Sb\,Zn_3$ which exhibits itself in a proneness of the crystals of $Sb\,Zn_2$ to

an excess of zinc. The line *k i* has been continued with dots in order to show that the influence of Sb Zn_3 extends as far as the alloy of 42·8 p. c. of zinc. On returning to the alloy of 31·5 p. c. of zinc and adding an excess of antimony it was fonnd that the crystals formed continued to have the theoretical composition of Sb Zn_2 until the amount of zinc in the alloy had fallen to 27 p. c., so that the tendency towards the theoretical composition was so great, that in the alloys between 31·5 and 27 p. c. of zinc, crystals were formed having very nearly this composition. On still further increasing the amount of antimony in the alloy, the composition of the crystals gradually approached that of the alloy, and from the alloy of 20·2 p. c. of zinc, very imperfect crystals were obtained having almost the same composition as the menstruum. At the same time, the crystals became less and less perfect and finally disappeared altogether in the alloys below 20 p. c. of zinc.

The portion of the curve *k m n h*, is the most important result of this investigation and therefore deserves especial notice. It has been shown that crystals of the form of Sb Zn_2, or at least crystalline scales of the same character, are formed in the alloys between 20 and 43 p. c. of zinc, the first per cent. corresponding to Sb Zn and the second to Sb Zn_3. Half way between these two points, that is the alloy of 31·5 p. c., is the point where crystals having the calculated composition of Sb Zn_2 are first obtained. Were the variations in the composition of the crystals of Sb Zn_2 exactly proportioned to the excess of zinc or of antimony in the alloy, as is the case with Sb Zn_3, then the curve of variation would be the straight line formed by the continuation of the line *a b*. From this line *b h* the course of the curve is deflected by the force which determines the union of the elements in definite proportions, and which for the want of a special term, I will call the Chemical Force. This is so strong that the curve runs parallel to the axis of ordinates through the distance *k m*. Beyond this point, the influence of the excess of antimony in the alloy becomes stronger than the chemical force, and the curve gradually bends towards the line *h b* which it finally meets at *h*. In the portion *h n* of the curve, the analyses are best represented by the arc of a circle, of which the radius equals *h e* or one-half of *h b*, and to which the line *k m* is tangent. In the portion *n m* the points determined by analysis may also be connected by the arc of a circle of which the radius *o′ n* equals the difference between the radius *o n* and twice *g n*, so that the two centres are at the same distance from the line *a h*. The whole curve is evidently the result of two forces; one acting along the chord in the direction *b h*, a force tending to increase the amount of antimony in the crystals proportional to the amount in the alloy, the same force in fact, which acts undisturbed in forming the portion of the curve *b a*; the other the chemical force acting in the di-

rection of the tangent *k m*. It has already been stated that crystals having the calculated composition of $Sb\,Zn_2$ are not first formed in the alloy of the same composition 33·5 p. c. of zinc, but in an alloy containing two per cent. less; so that the line *m k*, instead of extending to *e*, changes from this direction at *k*, and afterwards runs parallel to the line *b h*. Unless this fact can be explained by a tendency in $Sb\,Zn_2$ to an excess of zinc caused by the influence of $Sb\,Zn_3$ as suggested above, the reason of this difference between $Sb\,Zn_2$ and $Sb\,Zn_3$ in this respect is not clear; but as some evidence that it is not accidental it may be stated, that the distance *k c* equals *c i*, the last point being the one, at which the tangent line *m k* extended meets the curve. Another remarkable fact whose bearing cannot be at present seen, but which like the last serves to corroborate the general accuracy of the result was pointed out by my colleague, Prof. Peirce, after the plate had been engraved. The distances of the three most important points of the curve of $Sb\,Zn_2$ from the line *a h*, viz. *k d*, *m f*, and *n g*, are simple multiples of the first; *n g* is twice and *m f* three times *k d*. The curve has been fixed, as will be noticed from the dots, by a large number of points determined throughout the greater part of its length at every per cent., and in the portion *m n* at every half per cent.; they certainly coincide with the curve as closely as could possibly be expected, and the very agreement of so many different determinations by three separate analysts is a strong proof of the general correctness of the work.

By making hypotheses in regard to the nature of the two forces, which have generated the curve just described, it would not be difficult to obtain for it a mathematical expression; but as such hypotheses, in our ignorance of the nature of these forces, would be premature, I must content myself with giving its geometrical construction on a chart ruled like the plate illustrating the memoir. Let the coördinates of any point of the curve be, $x =$ per cent. of zinc in the crystals, and $z =$ per cent. of zinc in the alloy. In order to construct the curve of $Sb\,Zn_3$, find a point (*a*) of which $x = z = 43$ p. c. (the calculated per cent. of $Sb\,Zn_3$) and draw a straight line *a b* equally inclined to the two axes in the direction from the origin. To construct the curve of $Sb\,Zn_2$, produce the line *a b* in the opposite direction to the point $x = z = 20$, which will be the lowest point of the curve. Find next a point (*k*) of which $x = 33{\cdot}7$ p. c. (the calculated per cent. of $Sb\,Zn_2$ is 33·5) and $z = 31{\cdot}5$ p. c., which is one-half of $43 + 20$. Through this point draw a line *m k* parallel to the axis of ordinates and intersecting the line *a b h* at *c*. The line *m i* is the tangent, and the line *b h* the chord of the required arc. On the line *m i* take $c\,i = c\,k$, and *i* is the point at which the arc should touch the tangent. Erect a perpendicular on the tangent at the point *i*, take $o\,i = \frac{1}{2}\,b\,h$, and from *o* as a centre, with a ra-

dius $= o\,i$, describe the arc $h\,i$. Also from the centre o let fall a perpendicular $o\,g$ on the chord $b\,h$, and produce it to a point o' making $o'\,g = o\,g$. It will intersect the arc at (n). From o' as a centre with a radius $o'\,n$ describe a second arc $n\,m$ intersecting the tangent at m. Finally, draw from k, a straight line $k\,l$, parallel to $b\,h$, then the broken line $l\,k\,m\,n\,h$ will be the required curve.

It will be noticed that the tangent which has been drawn on the plate through the points determined by analysis is two-tenths of a per cent. in advance of the line which would correspond to $Sb\,Zn_2$. This position is essential to the equality of $k\,c$ and $c\,i$, if we retain as the value of the radius of the larger arc $R = \frac{1}{2}\,b\,h$. If the analyses should have given erroneously too much zinc so that the true position of the line should be at $x = 33{\cdot}5$ per cent., then this equality would be destroyed, and the conditions for finding the centre o would be reduced to the coördinates of the point h, the length of the radius and the position of the tangent, from which by a very simple construction the curve might be drawn. It should however be remarked that the position of the tangent in advance of the line $x = 33{\cdot}5$ is in accordance with the fact, already noticed, that the crystals of $Sb\,Zn_2$ have throughout a proneness to an excess of zinc caused apparently by the influence of $Sb\,Zn_3$; but it is also true that the tendency of the error in the zinc determinations is in the same direction.

Before discussing the conclusions to which the facts already stated seem directly to point, it will be well to see how far the variation in composition corresponds to a variation in the properties of the two compounds. Three classes of properties have been examined in this connection, viz., Specific Gravity, Crystalline Form, and Affinity for Oxygen, which will be treated of in order.

Specific Gravity.—The specific gravities of all the crystals analyzed, as well as that of the zinc and antimony used in the investigation, were taken with the greatest care. The determinations were made with a nicely constructed specific gravity bottle, as this method was found susceptible of greater accuracy than any other, when the temperature was observed with precision. In calculating the specific gravity, the weight of the water was corrected for the temperature, so that the unit is in all cases distilled water at 4° C. A similar correction could not be made for the temperature of the substance, as the coefficients of expansion of the crystals are not known. The results of the determination all made by myself are collected in the following table in the column headed "Sp. Gr. by Experiment." In the column headed "Mean Sp. Gr. of Zinc and Antimony" are given the cal-

Specific Gravities of Crystals, formed in the Alloys of Zinc and Antimony.

Composition of the Alloys.		Composition of the Crystals		Sp. Gr. of Crystals by Experiment.	Mean Sp. Gr. of Zinc and Antimony.	Expansion in Crystallizing.
Per ct. of Zn.	Per ct. of Sb.	Per ct. of Zn	Per ct. of Sb.			
100·00				7·153	7·153	0·000
*96·00	4·00			7·069	7·134	0·065
*86·20	13·80			6·898	7·086	0·188
*76·30	23·70			6·769	7·039	0·270
70·40	29·60	64·20	35·80	6·699	6·982	0-283
66·50	33·50	61·00	39·00	6·628	6·967	0·339
64·50	35·50	58·56	41·44	6·596	6·956	0·360
62·50	37·50	55·53	44·47	6·506	6·941	0·435
60·60	39·40	55·00	45·00	6·440	6·939	0·499
58·60	41·40	50·39	49·61	6·396	6·917	0·521
56·60	43·40	49·95	50·05	6·388	6·915	0·527
48·70	51·30	48·66	51·34	6·404	6·909	0·505
46·70	53·30	46·77	53·23	6·376	6·900	0·524
44·80	55·20	44·26	55·74	6·341	6·888	0·547
42·80	57·20	43·09	56·91	6·327	6·882	0·555
*40·00	60·00			6·386	6·867	0·481
*35·00	65·00			6·404	6·844	0·440
33·00	67·00	35·37	64·63	6·401	6·845	0·444
29·50	70·50	33·62	66·38	6·384	6·837	0·453
27·50	72·50	33·85	66·15	6·383	6·838	0·455
26·50	73·50	32·08	67·92	6·400	6·829	0·429
26·00	74·00	31·07	68·93	6·418	6·824	0·406
25·50	74·50	30·43	69·57	6·428	6·822	0·394
24·50	75·50	28·76	71·24	6·449	6·813	0·364
22·50	77·50	26·62	73·38	6·453	6·803	0·350
21·50	78·50	24·83	75·17	6·467	6·795	0·328
*15·00	85·00			6·564	6·748	0·184
*10·00	90·00			6·603	6·725	0·122
*5·00	95·00			6·655	6·701	0·046
	100·00			6·677	6·677	0·000

culated specific gravities of the same crystals on the supposition that the two metals had undergone no expansion on uniting. The last column was obtained by subtracting the numbers of the former from those of the latter, and therefore shows the relative amount of expansion. On examining the table, it will be found 1st. Than the union of antimony and zinc is accompanied by expansion. 2nd. That the specific gravity of the crystals varies slightly with the composition. 3d. That the two minimum specific gravities correspond precisely to the composition of $Sb\,Zn_2$ and $Sb\,Zn_3$, so that the specific gravity increases and the expansion diminishes as you depart on either side from these two centres. 4th. That the specific gravity of $Sb\,Zn_3$ is smaller than that of $Sb\,Zn_2$. We find then that the specific gravity determinations confirm in general the results of the analysis pointing out the same two centres of crystallization.

Crystalline Form.—It has already been stated that only two crystalline forms can be obtained from the alloys of zinc and antimony, that of $Sb\,Zn_3$ and that of $Sb\,Zn_2$. A large number of

* Alloys not crystallized.

crystals of $Sb\,Zn_3$ from different alloys, and therefore containing different proportions of zinc, were carefully measured for the purpose of ascertaining whether the angle was at all affected by the variation of composition. Fortunately four different crystallizations afforded excellent crystals, the angles of which could be measured to a minute. The crystals contained respectively 43·15, 44·14, 46·90 and 55·00 per cents. of zinc, and on all these by repeated measurements the angles were found to be *identical* with those given under figs. 1 and 2. Crystals from many of the other alloys were also measured, but on account of the imperfections of their surfaces the angles could not be determined within five or ten minutes. In all these cases however the values of the angles given above were included within the limits of uncertainty.

The faces of the crystals of $Sb\,Zn_2$ are not generally so perfect as those of $Sb\,Zn_3$, nor is their tabular form so well adapted for measurement; moreover variations in some of the angles have been noticed in crystals from the same crystallization amounting even to ten minutes. The angle 0 on 1 however appeared to be very constant for in all cases where it could be accurately measured the same value was obtained. As none of the crystals of $Sb\,Zn_2$, containing an excess of antimony, could be measured with precision, no constant variation of angle could be detected and on the other hand it could not be proved to be invariable.

Affinity for Oxygen.—The affinity of the crystals of $Sb\,Zn_3$, of different compositions, for oxygen, may be estimated by comparing the amounts of hydrogen gas evolved in a given time on boiling alloys of the same composition with water. The results of such experiments were given in the former memoir in a table, a mere glance at which will discover the two following facts—

1st, That up to 40 per cent no great increase in the amount of hydrogen evolved is obtained by increasing the amount of zinc in the alloy.

2nd, That at the alloy containing 42 per cent. of zinc there is an immense maximum confined at most between two per cent on either side.

General Conclusions.—Before stating the conclusions to which as I think the facts now established directly point, it will be well to consider the only two admitted principles of chemical science which could possibly be brought forward to explain similar variations. They are, first, that of impurities in crystals; second, that of isomorphous mixtures. It will not be difficult to show that the variations in composition of $Sb\,Zn_2$ and $Sb\,Zn_3$ cannot be caused by either of these principles.

It is a well known fact that crystals frequently take up impurities which are either dissolved or mechanically suspended in the

menstruum in which they form, and it might be supposed at first sight that the excess of zinc or antimony in $Sb\,Zn_3$ or $Sb\,Zn_2$, bore the same relation to their crystals that the sand does to the rhombohedron of calcite from Fontainebleau, or oxyd of iron and chlorite to crystals of quartz; but, in the first place, in all cases where a considerable amount of impurity is present the crystals are either imperfect or else the angle is considerably changed at times even as much as two or three degrees; and secondly, as such impurities are merely mechanical, the amount in the crystals would in all probability be proportional to the amount present in the menstruum at the time of their formation. Now in the crystals of $Sb\,Zn_3$, from the alloy of 60 p. c. of zinc, there is present an excess of zinc amounting to 15 p. c. and nevertheless the crystals are as perfect as, and their angles identical with, those obtained from the alloy of 43 per cent. In the crystals of $Sb\,Zn_3$ the excess of zinc is to a certain limit directly proportional to the excess in the alloy, but in those of $Sb\,Zn_2$ the excess of antimony is far from obeying this rule; and were the excess in both cases a mechanical mixture the variation in both cases would undoubtedly follow the same law: again, the crystals of $Sb\,Zn_3$, take up an excess of zinc but do not take up an excess of antimony, while those of $Sb\,Zn_2$ crystallize with an excess of either,—facts which are as inconsistent with the idea of mechanical impurity as the last: finally the form of the curve of $Sb\,Zn_2$ of itself alone proves that the excess of antimony in the crystals is not in the condition of mechanical impurity; for in that case the variation of composition would not be influenced, as the curve shows that it is, by the chemical force.

A theory that the variation in composition resulted from the mixture of two or more isomorphous compounds would be even less tenable than the one just discussed. For in the first place it would be necessary to assume the existence of two other compounds of zinc and antimony isomorphous with $Sb\,Zn_2$ and of one other, if not more, isomorphous with $Sb\,Zn_3$. Not only would such an assumption be contrary to all the analogies of chemistry and therefore require strong evidence to sustain it; but in the second place it can almost be demonstrated that no such compounds exist. The crystals having the calculated composition of either $Sb\,Zn_3$ or $Sb\,Zn_2$ are marked as has been shown by striking peculiarities, and with one possible exception similar peculiarities were not observed throughout the whole series of crystals which have been examined. The crystals containing 50 per ct. of zinc and of the composition of $Sb\,Zn_4$ were found to have a slightly smaller sp. gr., than those just above or just below them, but the difference is so small that it may be accidental, and as the crystals exhibited none of the other peculiarities, which characterize crystals having the calculated composition of $Sb\,Zn_3$ or

$Sb\,Zn_2$, I could not attach sufficient weight to the one circumstance to feel authorized in admitting a third compound of zinc and antimony. Admitting however the existence of $Sb\,Zn_4$ yet, as exactly the same angle has been observed in crystals containing 55 per cent. as on those containing 43 per cent of zinc, it would be necessary in order to explain the variation in composition by the principle of isomorphous mixtures, to assume the existence of still a third compound isomorphous with $Sb\,Zn_3$, and containing more zinc than $Sb\,Zn_4$, which would increase greatly the improbability of the theory in question. Again, the only probable compound of zinc and antimony containing less zinc than $Sb\,Zn_2$ would be $Sb\,Zn$; and it will be remembered that the crystals of $Sb\,Zn_2$ which contained the largest excess of antimony corresponded very nearly to this compound. In like manner the crystals of $Sb\,Zn_3$ which contained the largest excess of zinc corresponded very nearly to $Sb\,Zn_3$. If then the excess of antimony or zinc in the crystals of $Sb\,Zn_2$, arises from a mixture of isomorphous compounds, it must be that $Sb\,Zn_3$, $Sb\,Zn_2$ and $Sb\,Zn$ are isomorphous. That the first two are not isomorphous may be seen by turning back to the description of their crystalline form; and that there is no crystalline compound $Sb\,Zn$ is sufficiently proved by the fact that the crystals of $Sb\,Zn_2$, which correspond most closely to it, are so very imperfect that they would hardly be recognized as crystals did they not form the lower limit of a series. Several other facts pointing in the same direction might be added, but sufficient it is thought has been said to show that the variations of composition described in this paper can not be explained either by mechanical impurities in the crystals or by the mixture of isomorphous compounds.

In the absence of any known principle of chemical science by which the remarkable variations of composition, that have been demonstrated in this memoir, can be explained, the conclusion is almost forced upon us that zinc and antimony are capable of uniting and producing definite crystalline forms in other proportions than those of their chemical equivalents: in other words, that the law of definite proportions is not so absolute as has been hitherto supposed. The explanation then of the variation of composition which I would offer is: that it is due to an actual perturbation of the law of definite proportions produced by the influence of mass. I suppose for example that in the crystals of $Sb\,Zn_3$, containing 55 per cent. of zinc, the zinc and antimony are united in exactly the same way as in those containing 43 per cent., or in other words, just as if the equivalent of zinc were increased to 52·57, that of antimony remaining the same. In support of this position I would offer two considerations. The first is that if the variation is not caused by mechanical impurities or by the mixture of isomorphous compounds, we can conceive of no other explana-

tion for the phenomenon than the one offered. This of course is merely negative evidence; for although science as yet presents us with no principle for explaining variations of composition other than those which have been discussed, and although we can conceive of none others, it does not follow that others may not exist or may not hereafter be discovered; but, nevertheless, this consideration is important inasmuch as it meets an obvious objection, which would be urged against any new doctrine, which conflicts with a generally received canon of chemical philosophy. The second consideration has the character of demonstration. It is that the curve of variation is evidently generated by a second force counteracting directly the chemical force. This second force, as has been shown, is exerted by the excess of one or the other element present in the menstruum, and it may therefore be appropriately termed the force of mass. While the chemical force tends to make the curve a straight line parallel to the axis of ordinates, the force of mass would reduce it to a straight line making an angle of 45° with the axis; under the influence of both these forces it follows the arc of a circle between the two. Now I urge that the character of this curve proves that the chemical force has been directly influenced by what we have called, the force of mass, in the same way that the irregularities of the orbits of the planets prove that the force of gravitation exerted by the sun has been disturbed in its action by the influence of the other members of the system. As the details in the form of the curve have been fully discussed in the previous part of the memoir, it does not seem to be necessary to dwell upon this argument, and I would therefore without further comment offer the curve as it has been laid down on the plate as the proof of the validity of the explanation of the variation in composition here advanced.

It is worthy of remark that while the curve of variation may be said almost to demonstrate that the law of definite proportions may be disturbed in its action, it also most clearly sustains the integrity of the law itself; for, as may be seen on inspection, the chemical force is sufficiently strong to retain the curve of $Sb\,Zn_3$ parallel to the axis of ordinates through a variation in the menstruum of nearly five per cent., and it is only when the excess of antimony present in the alloy exceeds six per cent. that the force which it exerts becomes strong enough to disturb the action of the law. What the nature of the disturbing force is must be for the present a matter of theory. I am inclined to think that it is a phase of the chemical force itself, in the same way that the perturbations in the motions of the planets are a secondary result of the force of gravitation.

Accepting the view of the subject, which has been offered, it will be obvious that the very large extent of the variation in the

compounds of zinc and antimony is due to the very weak affinity between these elements. Were the chemical force stronger in proportion to the disturbing force the variation would be lessened; were it weaker, the variation would be increased. This is illustrated in the difference between the curve of $Sb\,Zn_3$ and that of $Sb\,Zn_2$. It is evident from the action of chemical agents on the two compounds, that one equivalent of antimony and two of zinc are united by a stronger force than one equivalent of antimony and three of zinc, and we find that the crystals of $Sb\,Zn_2$ retain the calculated composition under a considerable variation in the composition of the menstruum, while the composition of those of $Sb\,Zn_3$ varies with the slightest increase of the amount of zinc in the alloy.

To what extent this perturbation of the law of definite proportions prevails among chemical compounds it must remain for future investigation to determine. There are however a number of facts which tend to prove that it is very general whenever chemical affinity is weak. Four of these I will cite as being remarkably analogous to the facts under discussion.

1. Rieffel, to whose investigation of the compounds of tin and copper we have already referred, says, after the paragraph quoted in the introduction to this memoir, "Les aiguilles de $CuSn_{24}$ sont plus grosses que celles de $CuSn_{48}$". "*On croit, sans oser l'affirmer, qu'elles sont, par compensation, en nombre moindre, et que des différences analogues ont lieu dans les autres* $CuSn\varphi$ *à mesure que* φ *augmente jusqu' à* $\varphi=\infty$, *ou jusqu' à l'étain pur.*" It will be noticed that the difference between these needles is precisely the same as the difference between the crystals of $Sb\,Zn_3$ containing a small and a large amount of zinc, and I think that no one after reading Rieffel's paper can doubt that the compounds of copper and tin vary in composition like those of zinc and antimony.

2. The mineral Discrasite, a compound of silver and antimony, crystallizes in trimetric prisms, of which I on $I=119°\ 59'$.* The analyses given below are copied from Dana's System of Mineralogy, changing slightly the order.

$Sb\,Ag_3$ = Antimony 28·5 Silver, 71·5=100. $Sb\,Ag_4$ = Antimony 23, Silver 77=100.

1. Andreasberg (foliated granular),	Antimony	24·25	Silver	75·25=99.5,	*Abich.*
2. Wolfach (coarse granular),	"	24	"	76=100,	*Klaproth.*
3. Andreasberg (foliated granular),	"	23	"	77=100,	"
4. " " "	"	22	"	78=100,	*Vauquelin.*
5. Wolfach (fine granular),	"	16	"	84=100,	*Klaproth.*

It needs no comment on these results to show that Discrasite is homœomorphous with $Sb\,Zn_3$, and varies like it in composition.

* Dana's System of Mineralogy, 4th ed., vol. ii, p. 35.

3. In a paper recently published,* W. Sartorius von Waltershausen gives descriptions and then analyses of a new mineral occurring with Dufrenoysite in the Binnen Valley, Switzerland, in Dolomite. As the analyses do not agree with each other and do not correspond to a simple formula, von Waltershausen regards the compound as consisting of two hypothetical isomorphous compounds $PbS + AsS_3$ and $2PbS + AsS_3$ and calculates the proportions in which these compounds are mixed in the specimens analyzed. He infers that they are isomorphous from their analogy in composition to Zinkenite and Heteromorphite, $PbS + SbS_3$ and $2PbS + SbS_3$ which he regards as isomorphous. Prof. J. D. Dana questions the isomorphism of the last and thinks that the hypothesis that the new compounds are isomorphous requires further evidence.†

4. It is stated by Staedeler‡ that crystals of the compound of grape sugar and common salt can be obtained containing for every equivalent of grape sugar one or two equivalents of chlorid of sodium and also of intermediate composition. He states moreover that "Calloud, who first observed that the grape sugar of honey combined with chlorid of sodium, found that the amount of the latter varied between 8·3 and 25 per cent." Staedeler refers the variation in composition to a mixture of the compound of one with the compound of two equivalents of chorid of sodium which he assumes to be isomorphous. He adds that it may be caused by "enclosed crystals of chlorid of sodium although the eye could not distinguish any heterogeneous constituents."

All the above compounds are examples of weak chemical affinity accompanied by large variations in composition without any change in the general crystalline form. It is not meant to assert that the variations are identical in character with those of $SbZn_3$ and $SbZn_2$, but only that there is a strong probability that this is the case, which in the first two instances amounts almost to a certainty.

If variations in composition of such magnitude are possible when the force of chemical affinity is weak, it is highly probable that some variation may occur when the force is strong, and, whatever view may be taken of the cause of the variation it will now become a matter of importance to ascertain whether many discrepancies in analyses hitherto referred to imperfections in the process, may not be owing to the same cause which influences the composition of the crystals of zinc and antimony. For this purpose, it will be best to make several analyses of the same compound, prepared under circumstances differing as widely as possible, and then to apply to the results "Peirce's Criterion for

* Poggendorff's Annalen, vol. xciv, p. 115.
† American Journ. of Science, vol. xix, p. 355.
‡ Chemical Gazette, vol. xiii, p. 44.

the rejection of doubtful observations." Such investigations will be greatly simplified by tables prepared by Dr. B. A. Gould* for facilitating the application of this criterion to which I would refer all chemists who are inclined to take up this line of investigation.

I am well aware that in announcing the existence of perturbations of the law of definite proportions I am calling in question one of the most fundamental dogmas of chemical philosophy, and that the new doctrine will have to encounter prejudice on this very ground. This law is so intimately associated in many minds with the atomic theory, that, to such, absolute definiteness seems to be its essential characteristic; nevertheless, I can not but believe that, laying aside the prejudices which the theory begets, it will be seen by all, that the analogies of nature support the doctrine of variation as maintained in this memoir. The phenomena of some of the phenomenal† laws of nature have that definiteness of character which is claimed for those of the chemical law. The planetary orbits are not perfect ellipses. The ratios of the harmony scale are but approximately realized. The arrangement of leaves on the stem is not perfectly regular. Isomorphism is seldom absolute. In all we observe only a tendency towards a maximum effect which is the perfect expression of the law, but which is rarely fully reached. The limits of variation are broader in some instances than in others, but we find no case in which there is absolutely none. This same character which pervades the other phenomenal laws of nature, I claim for the great law of chemistry. The definite proportion I regard as a maximum toward which the chemical force strives, a maximum, from which the deviations in most cases are small, although in others it may be very large; and I maintain that this view of the subject, which the memoir has aimed to establish, is supported by the analogies of nature.

When the dynamical law has been discovered, of which the phenomenal law was merely the outward manifestation, as Kepler's laws were merely the phenomena of the law of universal gravitation, the very variations have been seen to be necessary consequences of the law itself, and if even the dynamical law, which governs chemical phenomena, shall be discovered, it is most probable that the variations from the law of definite proportions will become as much a matter of calculation as the perturbations of Astronomy. In both cases the perturbation is apparently due to the influence of an extraneous mass of matter.

* Astronomical Journal, vol. iv, p. 81.

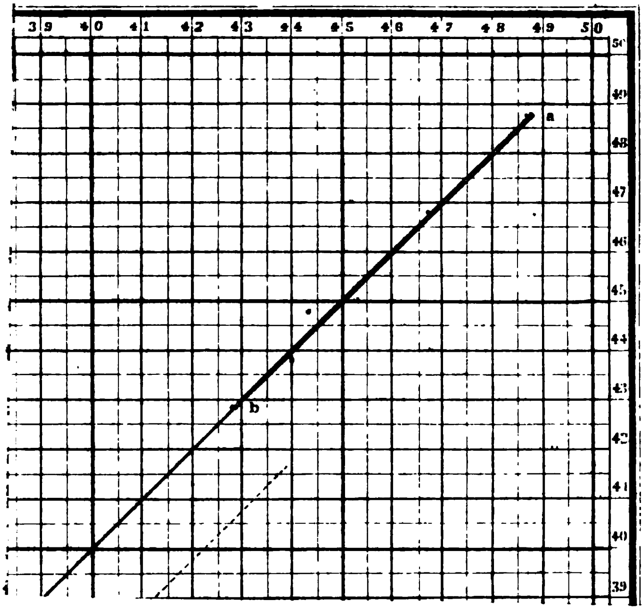
† I have used the term phenomenal laws to designate a class of laws of nature which are empirical in their character inasmuch as they are obviously not ultimate, although their deviation has not been discovered, but which are more universal than those to which the term empirical is commonly applied.

The argument from analogy becomes stronger, when we consider the equivalent numbers. I have shown in a former memoir* that these numbers may be connected by a very simple numerical law, but here, as in other cases, we find merely a tendency towards the law, not an absolute agreement with it, the differences between the theoretical and the experimental equivalents being in many cases too great to be covered by errors of observation. The present memoir may throw light upon these discrepancies; for, to say the least, it is possible that the differences may originate in variations of the equivalent itself, and that the theoretical equivalent may be the maximum towards which the chemical force tends. On comparing carefully the different determinations of the chemical equivalents, many facts may be noticed supporting this view; those equivalents for example, which coincide with or very nearly approach whole numbers such as those of oxygen, carbon and sulphur, will be found as a general rule to have been determined by the analysis or synthesis of compounds whose elements are united by a strong force; also when the equivalents have been determined by essentially different processes it will be noticed that they seldom perfectly agree; so that whatever view may be taken of the subject it will now become a matter of the highest importance to ascertain how far; if at all, the determinations of the chemical equivalents have been influenced by similar causes to those which have produced the variations described in this memoir. This influence can only be detected by multiplying the determinations, by as many different processes as possible, and submitting the results to a rigorous mathematical scrutiny.

If the doctrine of this memoir is correct and the chemical equivalents are really liable to variation it will have an important influence on chemical philosophy. The atomic theory as at present interpreted by chemists is irreconcilable with it, and our present ideas in regard to isomorphism must be materially changed. But it must be remembered that the conclusions of the memoir are drawn from the examination of only two compounds, and therefore that it would be premature to dwell on these obvious consequences of the principle until it has been substantiated by further investigations. In conclusion, I would express my obligation to the gentlemen who have assisted me in the labor of the investigation which on account of the large number of analyses has been very great and could not have been concluded so soon had it not been for their great industry and zeal.

* This Journal, vol. xviii, p. 229,

IN THE ALLOYS OF ZINC AND ANTIMONY.



between such a mixture and a true chemical compound. Admitting, then, the possibility of a variation of composition in a mineral species, independent of the phænomena of isomorphism, it becomes of importance to distinguish this new class of phænomena by a separate term; and I would propose for this purpose the word *Allomerism*. By this word I would designate *a variation in the proportions of the constituents of a crystallized compound without any essential change in the crystalline form.* If, then, we also use the word *typical* to indicate the condition of *definite composition*, we may speak of those specimens of a mineral species which contain an excess of one or the other constituent, as *allomeric variations from the typical composition.* The degree of allomerism would then be measured by the excess of the *allomeric constituent* above the typical composition. Thus the crystals of $Sb\ Zn^3$ containing 42·3 per cent. of zinc would be said to have the typical composition; while those containing 55 per cent. of zinc would be distinguished as an allomeric variety, the degree of allomerism in this instance amounting to 12 per cent., and zinc being the allomeric constituent. In the case of the mineral Discrasite, it is probable that no specimen having the typical composition has yet been analysed. Those specimens whose analyses are given in Dana's 'System of Mineralogy,' are all probably *allomeric varieties* of the mineral, silver being the allomeric constituent, and the degree of allomerism varying from 4 to 7 per cent. It is unnecessary, however, to multiply examples, as the above are sufficient to illustrate the use of the term.

[From the American Journal of Science and Arts, Vol. XXXI, March, 1861.]

ON THE DIMORPHISM

OF

ARSENIC, ANTIMONY AND ZINC.

By JOSIAH P. COOKE, Jr.

The rhombohedral forms of arsenic, antimony and zinc are well known. Those of arsenic and antimony have been determined by several observers,* and that of zinc first observed by Nöggerath,† on a furnace product from the smelting works of the Vieille Montaigne Zinc Co., near Aix la Chapelle, was subsequently redetermined on the same specimen by Gustav Rose.‡ It is the object of the present paper to show that these elements may also crystallize in regular octahedrons and therefore that they are dimorphous. Supposed monometric crystals both of arsenic and zinc have been previously described but since these observations have been discredited, the author has thought it best to publish his results.

Arsenic.—In the "Journal für praktische Chemie," vol. xxii, 344, 1841, Elsner describes, as crystals of arsenic, octahedrons, which he obtained by subliming a mixture of arsenious acid and charcoal powder. The author repeated the experiment of Elsner and obtained very distinct octahedral crystals, having a nearly black color and bright lustre, which were undoubtedly the same as those observed by Elsner. Similar crystals made by subliming the commercial arsenic, "cobalt," in a glass flask were at first sight mistaken by the author for crystals of arsenic. Their true

* See description of a crystal of rhombohedral arsenic, in Proceedings of American Academy of Arts and Sciences, vol. iii, 86.
† Poggendorff Annalen, vol. xxxix, 323.
‡ Poggendorff Annalen, vol. lxxxiii, 129.

nature however became evident on boiling the crystalline mass in water when it all dissolved with the exception of a small quantity of a black amorphous powder, the amount varying with different specimens. The substance dissolved was easily recognized as arsenious acid, and the black powder as finely subdivided metallic arsenic. The octahedrons were evidently merely crystals of arsenious acid containing as a mechanical mixture, particles of metallic arsenic like the sand in the crystals of Fontainbleau limestone. This result led the author to make a series of experiments with a view of testing the possibility of crystallizing pure metallic arsenic in forms of the monometric system. In one experiment rhombohedral crystals of arsenic, which had been prepared by sublimation in the usual way, afterwards kept under water, deprived of air by boiling, and just before using dried in a current of hydrogen, were introduced into a glass flask. Through this flask which was fitted with a cork and glass tubes for the purpose, a gentle current of hydrogen was maintained, the gas entering at the top and passing out near the bottom of the flask. As soon as the flask was known to be filled with hydrogen, the arsenic was sublimed in this atmosphere, when it condensed around the neck forming the well known metallic mirror. On subsequently breaking the flask and examining the mirror with a microscope (power of eighty diameters) it was found to be studded with distinct octahedral crystals having a greyish color and a bright metallic lustre. These octahedrons were recognized as belonging to the monometric system first by measuring the angles of the triangular faces and finding that they were equilateral triangles, second by the general "habitus" of the crystals especially in their distorted forms which could never be mistaken for truncated rhombohedrons, the only form with which they were liable to be confounded. The crystals were strictly microscopic and could not be distinguished with a pocket lens except as brilliant points. The precautions taken in the preparation seemed to exclude the possibility of any arsenious acid being present, but in order to establish this fact beyond a doubt, a portion of the metallic crust studded with the crystals was boiled in water for several minutes and afterwards treated with the strongest aqua ammoniæ for twenty-four hours, but the crystals were not dissolved by either reagent nor was their sharpness apparently impaired.

In another experiment arseniuretted hydrogen gas was reduced in a bohemian glass combustion tube in the usual way, when testing for arsenic only on a larger scale and with special precaution in order to ensure the exclusion of air from the apparatus, and to regulate the quantity of arseniuretted hydrogen in the current of hydrogen gas. To one end of the combustion tube was connected by a cork a small exit tube whose open end dip-

ped under mercury the other end was connected by means of a tube having two branches each provided with a stop-cock with a hydrogen generator on the one hand and on the other with a gas bottle generating arseniuretted hydrogen. The last was provided with a safety tube by which the excess of gas not needed in the experiment might escape. Before heating the combustion tube it was filled with hydrogen from the generator by which a uniform current of gas through the tube was maintained during the process. A portion of the tube two or three inches long was next heated to a red heat and then by opening the stop-cock a very small amount of arseniuretted hydrogen was allowed to mix with the hydrogen current and the experiment continued until a metallic mirror was formed on the glass beyond the heated portion of the tube. This mirror examined by the microscope, was found to be studded with minute octahedral crystals, which were submitted to the same test as before and with the same results.

Antimony.—No crystals of this metal except the well known rhombohedral forms ever appear to have been observed. Hauy formerly supposed that he had discovered in antimony the four cleavage planes of the regular octahedron and the six cleavage planes of the regular rhombic dodecahedron, but his observations were made on the ordinary regulus of antimony, which is now known to have rhombohedral cleavages. After crystallizing arsenic in octahedron by the process last described the author succeeded in obtaining octahedral crystals of antimony with the same apparatus, using antimonuretted hydrogen in place of arseniuretted hydrogen. The tube was heated with a Bunsen's gas burner to as high a temperature as it was capable of yielding and the process conducted as before. On breaking the tube and examining the metallic mirror with a microscope it was found studded with minute octahedral crystals. They were more readily obtained than the corresponding crystals of arsenic and presented the same characteristic forms. The solid angles of the octahedrons were very frequently observed modified by the faces of the cube and in one case at least the edges were truncated by the faces of the rhombic dodecahedron. These modifications are of importance as they remove all doubt in regard to the system of crystallization. The crystals being microscopic their interfacial angles could not of course be measured, but the existence of these modifications is even more satisfactory evidence on this point than an actual measurement.

It is well known that oxyd of antimony is capable of crystallizing in octahedrons belonging to the monometric system and although from the construction of the apparatus it was deemed impossible that any sensible amount of air could become mixed with the hydrogen in the tube, yet in order to remove all doubt

on the subject, the crystals were exposed to the following reagents.

A portion of the glass tube covered with crystals was first boiled for a long time in water and subsequently treated with the strongest liquid hydrochloric acid; but although exposed to the action of the acid for several days in a warm room, the crystals were not dissolved. They also resisted for some time the action of boiling hydrochloric acid, but after prolonged boiling they disappeared. Exposed to the action of chlorine gas at a very gentle heat, the crystals were immediately consumed, leaving no residue and rendering the gas cloudy from the fumes of chlorid of antimony. Lastly, a portion of the tube (on which was deposited nothing but distinct octahedral crystals), was treated with a few drops of nitric acid, and a gentle heat applied. The crystals were at once attacked and the familiar white powder of antimonious acid was the result. This dissolved on adding a few drops of hydrochloric acid and the solution evaporated nearly to dryness, diluted with a solution of tartaric acid and subsequently treated with a solution of sulphid of hydrogen, gave the familiar red precipitate of sulphid of antimony.

In the metallic mirrors of arsenic and antimony obtained by Marsh's test, the metals seem to be always in the octahedral modification, and when deposited slowly are more or less crystalline. The author has obtained the best crystals by resubliming the metallic mirrors, after they were first formed, in a slow current of hydrogen, and it is in this way very easy to obtain the crystals entirely isolated on the surface of the glass tube, and in the case of antimony the author has traced with the microscope every gradation between the distinct crystals and the granular coating, which forms the mass of the mirror. The process of crystallization in the formation of the mirror is similar to that of salammoniac on a glass plate and the lines of crystals shoot out in the same way parallel to the axis of the tube.

Zinc.—In the "Annales de Chimie et de Physique," vol. xxii, 37, 1848, Nicklès has described some crystals of pure zinc prepared by M. Favre with the process of M. Jacquelain as pentagonal dodecadrons but unfortunately he has given no measurement of angles to confirm his opinion. This observation has been questioned by Gustav Rose* on the grounds first that the mamilary concretions of zinc, which are frequently deposited on the cooler portion of the retort during the process of distillation might readily be mistaken for pentagonal dodecahedrons without any exact measurement of angles, and secondly that this form which is characterized by a peculiar law of symmetry, has never been observed unless this case is an exception, on any metallic crystals. The question might readily be settled by a reëxamina-

* Poggendorff, Annalen, vol. lxxxv, 298.

tion of the original specimen and it is to be hoped that, if they still exist, such an examination will be made.

In "Poggendorff's Annalen," vol. cvii, 441, 1859, Gustav Rose has described two specimens of crystallized brass formerly belonging to the mineral collection of Klaproth, which show in the cavities of the mass distinct crystals. Rose infers that these crystals belong to the monometric system rather from their grouping as indicated by the striation than from the external forms of the individual crystals which was too indistinct to admit of exact determination. This subject has been much more fully studied by Mr. F. H. Storer in the laboratory of Harvard College. Storer obtained octahedral crystals composed of zinc and copper in the varying proportions of the constituents from pure copper to 70 per cent of zinc. The crystals were made by fusing the metals in a crucible and pouring out the still liquid alloy after a crust had formed on the surface as in crystallizing bismuth or sulphur. They were all too ill-defined to admit of direct determination and although they exhibited similar striations to those described by Rose, the striæ did not seem to the author to fix the system of crystallization with such clearness as to exclude all doubt. There were however other circumstances which were thought to point out the system of the crystals; first, the crystals resembled precisely the artificial crystals of magnetic oxyd of iron which are frequently obtained as a furnace product, and which are known to belong to the monometric system. The author had recently the opportunity of comparing with the brass crystals a very finely characterized specimen of this magnetic oxyd in the mineral collection of Dr. Krantz at Bonn. Second, the whole series of crystals including those of pure copper had the same characters and if the crystals of copper were monometric, as no one will question, the rest are also. But assuming that the octahedrons in question are monometric, this fact has no bearing upon the crystallizing form of zinc unless it can be also shown that there is no definite chemical combination between the zinc and the copper, or in other words, that the alloys of those metals are nearly isomorphous mixtures. Storer has proved this point as the author thinks, conclusively, by analyzing the series of crystals as well as the alloys in which they were formed. The full details of his results will be found in his memoirs in vol. vi of the Memoirs of the American Academy of Arts and Sciences. It is sufficient for the present purpose to state that the composition of the crystals was in every case sensibly the same as that of the alloy.

This investigation seems to prove that zinc is capable of assuming a monometric condition and thus of crystallizing in connection with copper in the same way that sulphate of copper may be made to crystallize in connection with sulphate of iron, taking

the form of green vitriol although it generally assumes the form of another system. But although his results are conclusive as far as they go, Storer could not obtain crystals containing more than 70 per cent of zinc. The alloys of zinc and copper containing more than this per cent of zinc become granular on cooling, and do not yield distinct crystals. The following observations of the author may therefore be of value in extending the history of the subject.

During the course of some experiments on the compounds of zinc and arsenic a furnace product was accidentally obtained composed of these two elements imperfectly fused together and mixed with cinders. The cavities of this mass were lined with very brilliant octahedral crystals having a bright metallic lustre. The crystals although small could be easily measured with a reflective goniometer and gave the exact angle of the monometric octahedron. A sufficient number of the crystals for analysis was separated with some difficulty from the gangue. They were dissolved in dilute hydrochloric acid and the zinc precipitated with carbonate soda was determined in the usual way. The result gave

Zinc,	81·18
Arsenic,	18·82
	100·00

The quantity of arsenic in these crystals is so much smaller than the amount required to form any probable definite compound that there can be but little doubt that it is present as impurity and that the octahedrons are an isomorphous mixture of the two elements. The presence of a certain amount of impurity seems to favor metallic crystallization and it is possible that it may be the disposing cause in this case, inducing as it were a monometric condition in the zinc. The beautiful lead crystals containing a small quantity of antimony which are obtained at the smelting works near Clausthal in the Harz, are familiar to mineralogists, and the author has found that a small quantity of lead on the other hand greatly facilitates the crystallization of antimony. Similar facts have been noticed in the case of bismuth so that distinct crystallization instead of being the test of purity in the case of a metal is quite the reverse. To what extent the presence of these impurities may effect the crystalline form of the metal has not yet been determined but it is certain that this influence is important and that it depends as well on the amount as on the nature of the impurity. Laurent and Holms (Ann. de Chimie et Phys., [2], vol. lx, 333), state that zinc containing a few per cent of iron crystallizes in rhombic prisms, and Warren de la Rue also (Philosophical Magazine, vol. xxvii, 370) has analyzed and measured rhombic prisms of zinc having the composition, zinc

90·00, iron 2·56, lead 6·00, copper 1·44. Acicular crystals having a similar composition have also been described by Erdmann, (Berzelius, Traité, ii, 620). Morever the author observed in a furnace product similar to the one above described some flexible acicular crystals which he analyzed and found to consist of zinc 91·3, arsenic 8·7. These crystals could not be crystallographically determined but they were undoubtedly similar in form to those before described and entirely different from the octahedral crystals noticed above. Is it not possible that all the prismatic crystals of zinc, which have been described, including those of Nöggerath and Rose, may belong to the same crystalline system? If so the apparent anomaly presented by the above facts would disappear, and as the observers themselves do not claim that the crystalline system has in either case been determined beyond a doubt, this is not an improbable supposition; moreover the authority for the rhombohedral system rests on a single specimen, which, as Rose admits, is not capable of exact determination crystallographically and has never been analyzed. However these facts may be regarded, the octahedral crystals above described appear to the author to confirm the view that zinc is capable of crystallizing in the monometric system, but he does not attach to the observation any weight except as confirming previous results, and as furnishing additional data for the solution of the problem.

Cambridge, Nov. 14, 1860.

From the Author.

Contributions to Chemistry and Mineralogy

FROM THE

LABORATORY OF HARVARD COLLEGE,

BY

JOSIAH P. COOKE, Jr.

ERVING PROFESSOR OF CHEMISTRY AND MINERALOGY.

I. ON CERTAIN LECTURE EXPERIMENTS, AND ON A NEW FORM OF EUDIOMETER.

II. A METHOD OF DETERMINING THE AMOUNTS OF PROTOXYD OF IRON IN SILICATES NOT SOLUBLE IN THE ORDINARY MINERAL ACIDS.

III. CRYSTALLOGRAPHIC DETERMINATION OF SOME AMERICAN CHLORITES.

[From the American Journal of Science and Arts, Vol. XLIV, Sept. and Nov., 1867.]

NEW HAVEN:

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1867.

I.—ON CERTAIN LECTURE EXPERIMENTS, AND ON A NEW FORM OF EUDIOMETER.

THE laws of combination by volume fill such an important place in our modern chemical philosophy that simple methods of illustrating these fundamental principles in the lecture room are eagerly sought by every teacher of the science. The many new and interesting experiments devised for this purpose by Prof. Hofmann, first described in the Journal of the Chemical Society of London (Ser. II, vol. iii, page 156), and subsequently made still more widely known through his admirable "Introduction to Modern Chemistry," leave little to be desired so far as regards accuracy of results or elegance of illustration. But these experiments require for the most part a delicacy of manipulation, which is incompatible with the hurry of the lecture room, and a skill in glass-blowing which can rarely be attained or commanded by our American teachers. Hence while seeking the same end as Professor Hofmann, but with less ample appliances, the author has devised for his own lecture-room methods of illustrating the same principles, which require less delicate apparatus and less careful attention, although as analytical methods they may not always be as accurate as those of this eminent German chemist. Following also the recommendation of Prof. Hofmann in the article just referred to, the author publishes his methods with the hope that they may serve to bring the illustrations of these fundamental laws of chemistry within the reach of the great body of teachers in this country.

Many of the methods described in this paper are alone rendered possible by the application of vulcanized rubber stoppers in the construction of the required apparatus. Hitherto these have not been made of good quality in this country, and those imported from Europe were very costly, and could only be obtained of a few invariable sizes. At the suggestion of the author, the "Boston Belting Co." now manufacture an excellent article, which they call "stopper cord," consisting of conical rolls of very elastic rubber, about 4 feet in length and varying in diameter from one-half an inch at one end, to an inch and a half at the other.* From these rolls, stoppers of any required

* After a good deal of experience, rolls of the sizes named above have been found to be the most universally applicable, but they can be made to order of any desired dimension and at a cost not exceeding one dollar a pound. See fig. 5, where one of these rolls is shown in the fore-ground of the wood cut.

size between the limits named may be cut with an ordinary knife and bored with a common brass cork-borer. It is only necessary to moisten the tools with water in order to prevent the adhesion of the rubber. Stoppers of this material are absolutely air-tight even against a full atmospheric pressure, provided that the surface of adhesion to the glass neck is at least half an inch in length.

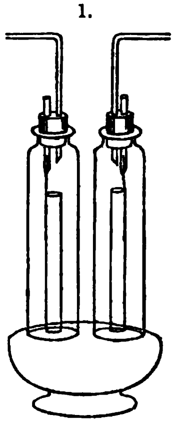
Another material of prime importance in these experiments is sodium amalgam, which is most conveniently used when containing so large an amount of sodium as to form a hard solid. It is best prepared by gently heating a few ounces of metallic mercury in a shallow iron dish and then cautiously adding one-twentieth of its weight of sodium. The first half of the sodium should be added in very small portions at a time as the action at the beginning is exceedingly violent, but soon moderates, and at last the melted amalgam must be stirred with an iron spatula in order to incorporate thoroughly the materials. As soon as cold the solid amalgam readily separates from the dish, and should then at once be broken up into small fragments and preserved in a well stoppered bottle.

The four great typical compounds of modern chemistry are HCl, H_2O, H_3N and H_4C. Excepting the last, for which we have no new methods, we will now describe our methods of illustrating the composition of each of these in turn.

Hydrochloric acid.—The points to be illustrated in the case of this gas are all indicated by the equation $\boxed{H} + \boxed{Cl} = \boxed{HCl}$ or by the molecular expression

$$\boxed{HH} + \boxed{ClCl} = \boxed{HCl}\,\boxed{HCl}$$

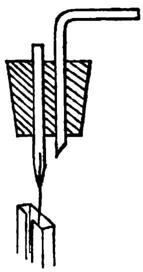
1.



The first fact that HCl consists of hydrogen and chlorine gases we prove by the electrolysis of strong liquid hydrochloric acid, having previously shown in the course of the lecture how HCl is obtained from common salt, and that the liquid acid is merely a solution of the gas in water. The decomposing cell, which we use in this experiment, is represented in outline by fig. 1, which is drawn to a scale of $\frac{1}{5}$, so that both its construction and dimensions require no detailed description. The two small open glass cylinders are fitted by grinding with emery to the two tubulatures of the cell, and when the instrument is not in use are closed above with ground glass stoppers. When mounted for use the cell is filled with strong hydrochloric acid to within an inch of the upper mouths of the cylinders, and the glass stoppers are replaced

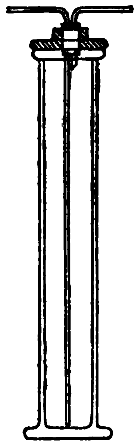
by rubber stoppers, through which pass the gas delivery tubes and the conducting wires connecting with the electrodes, which are two strips of platinum foil four inches long by one inch wide. The platinum conducting wires are welded* to the strips of foil and secured in the rubber stoppers as represented in detail by fig. 2. Into the lower end of a short piece of glass tube, which passes tightly through the rubber, the platinum wire connecting with the foil is secured by melting the glass around it, while the upper end is left open to receive the copper conducting wires from the battery, and the connection is made perfect by placing a few drops of mercury in the tube. This simple form of connecting-cup is easily made and very convenient.

2.

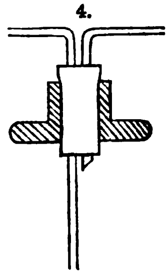


As the conducting power of hydrochloric acid is very good, three Bunsen cells of the ordinary size have ample intensity and give a rapid evolution of gas. The hydrogen gas is conducted into a tall but narrow glass jar mounted in the usual way over a small pneumatic trough, while the chlorine is collected by displacement in a precisely similar jar mounted as represented in fig. 3. The mouth of this jar is closed by a ground glass plate, which is tubulated, as is shown in detail by fig. 4. This tubulature again is closed by a rubber stopper, through which pass first, the delivery tube, which reaches the bottom of the jar, and secondly an overflow tube which merely passes through the stopper, and which in the experiment should be connected by a flexible hose with a ventilator. When a larger amount of chlorine is desired the first jar may be connected with a second, and that with a third, etc., all mounted in the same way, and the exit tube from the last jar leading to a ventilator as before. When the jars are full the tubulated stoppers with their connections are removed and a plain glass cover substituted. This simple form of apparatus will be found very useful in all experiments on gases heavier than the air.

3.



4.



During the process of electrolysis the class will see that the two gases are evolved in nearly the same proportions, the col-

* The platinum wire is very easily welded to the foil on a smoothed surface of a lump of quick lime which serves as an anvil. The two having been placed together in the required position on this support are first intensely heated at the points to be united, with a blow-pipe flame, and then a quick blow with a small hammer completes the work.

ored gas rising in one jar as rapidly as the water falls in the other. The narrowness of the jar prevents to a great degree the diffusion of the chlorine, and a piece of white paper placed behind the jar, will make the line between the colored gas and the air visible to a considerable distance. When the jars are full, the qualities of the two gases may be made evident by appropriate experiments. As is well known, the gases will not be delivered in atomic proportions, until the liquid acid is saturated with chlorine. It is best therefore not to empty the cell after the experiments, but, having removed the rubber stoppers with their attachments, to close the mouth with the ground glass stoppers, and the apparatus will then be ready for the next occasion. It is also best to interpose a small wash bottle containing sulphuric acid, between the cell and the chlorine jar, for this will not only dry the gas but also equalize the hydrostatic pressure on the two delivery tubes. Decomposing cells like that represented in fig. 1, and all other forms of glassware described in this paper are made by the New England Glass Co., of East Cambridge, and can be ordered through any of the dealers in philosophical apparatus in Boston. A much simpler decomposing cell, although not quite so efficient an apparatus, can be made with a common U tube supported on a wooden stand and mounted with rubber stoppers, delivery tubes and platinum electrodes in every respect like the other.

The second point to be illustrated in regard to hydrochloric acid is, that it consists of equal volumes of its constituent gases; and although by our first experiment, if made in the way we have described, it is shown that the gases are evolved in nearly equal proportions, yet a second experiment is required to establish the absolute truth* of this important fact. The apparatus we use for this purpose is represented in fig. 5, and the details of the several parts are shown in fig. 6. The two gases are evolved together from a simple decomposing cell, shown more in detail in fig. 9, but in connection with another apparatus, and the connection of the battery with the two electrodes, is here made as before shown in fig. 2. The mixed gases pass through a small drying tube filled with pumice moistened with oil of vitriol, into an absorption tube whose construction is shown in detail by fig. 6. As the gaseous mixture is decidedly lighter than air, it is conducted to the top of the absorption tube through the small quill tube, and overflows through the short tube below. Both of these should pass air-tight through the rubber

* We here of course leave out of view the small difference which arises from the fact that the gases do not absolutely obey Mariotte's law and are therefore unequally condensed even by the atmospheric pressure. The volumes of the two gases would undoubtedly be exactly equal under greatly diminished pressure, but under the pressure of the air, the volume of the molecular weight of chlorine is about $\frac{1}{100}$ less than the corresponding volume of the molecular weight of hydrogen, a difference by no means inappreciable in accurate experiments.

stopper, which closes the mouth of the large absorption tube and which should therefore have a bearing on the glass of at least half an inch. It will be noticed that while the overflow tube

5.



6.



is straight, the delivery tube is bent so that its open end is four or five inches above the mouth of the absorption tube. Rubber stoppers, or rather caps, must also be provided, by which the open ends both of the delivery and the overflow tubes may be closed at the right time. These are made by boring with a cork-borer *nearly* through an ordinary stopper and then pulling out the rubber core with a pair of pincers. The absorption tube should now be divided into two parts of equal capacity by means of rubber rings having however a length of three or four inches at the lower end for the absorbent liquid.

The absorption tube having been prepared as described and filled with the mixed gases, the experiment is made in the following way. The apparatus is first rapidly depressed in a solution of caustic soda (of the ordinary strength used in the laboratory) until the liquid rises in the tube to the level of the first ring. The open end of the delivery tube is now quickly closed with the rubber cap, and then the end of the overflow tube is closed in the same way—the second rubber cap having been previously dropped upon the bottom of the glass vessel containing the soda solution so as to be ready for the purpose. The tube,

now perfectly air tight, is removed from the liquid and the solution of soda turned backward and forward through its entire length until the chlorine is wholly absorbed. The end of the overflow tube is now opened under water colored blue with litmus, which, as it rushes in, will be instantaneously bleached, indicating the presence of chlorine. The tube must now be immersed in the water until the level of the liquid is the same within and without, when it will be found that just one-half of the gas has been absorbed. We have now proved that one-half of the volume of gas evolved during the electrolysis of hydrochloric acid consists of chlorine, and it only remains to show that the remaining half still left in the tube is hydrogen. For this purpose the delivery tube may be connected with a water faucet and the gas burnt as it is forced out through the overflow tube.

We have now proved first, that hydrochloric acid is composed of hydrogen and chlorine; secondly, that these gases are present in equal proportions by volume, and in order to complete our demonstration of the constitution of this typical compound, we have only to prove that when these equal volumes unite to form HCl there is no condensation. This we may do either synthetically or analytically.

The synthetical experiment is made by filling the absorption tube as before with the mixed gases obtained by the electrolysis of hydrochloric acid, taking great care, as also in the previous experiment, that the tube should be perfectly dry. It will of course be necessary to have two of these tubes if both experiments are to be made in the same lecture. The tube thus filled is to be exposed for some time to bright diffused sun-light, and afterwards directly to the sun-beam until perfect combination results. If the glass is quite thick, and the rubber stopper is forced in very tight, the gases may even be exploded in the tube without danger, although this form of the experiment is always attended with some risk. When the gases are in either way thoroughly combined, the end of the exit tube is first opened under mercury, in order to prove that no condensation has taken place, and afterwards under water colored blue by litmus, when a very rapid absorption takes place, and the reddening of the water will indicate that HCl has in fact been formed.

The analytical experiment is made by decomposing HCl gas by means of sodium amalgam. For this purpose the carefully dried gas is first collected over mercury in a perfectly dry tube. This tube we assume is graduated, or at least divided into two parts of equal capacity. The tube full of gas is now slipped over the mouth of a rubber cap, which has been previously filled with the amalgam, see fig. 5 (left side of the wood cut), and

sunk in the mercury trough until the liquid is just level with the brim. This cap, which is easily made from the "stopper cord," should be capable of holding ten or twenty cubic centimeters of the amalgam, and should tightly clasp the tube. Moreover for this purpose the solid amalgam, above described, should be reduced with mercury to the consistency of a thin paste. The amalgam is now to be shaken up in the tube for several minutes until the decomposition is complete, and then the mouth of the tube may be opened under mercury. The liquid will rise to supply the place of the chlorine which has been absorbed, and on sinking the tube in the mercury trough until the level is the same within as without, it will appear that exactly one-half of the volume has disappeared. As this, however, would require a deep cistern of mercury, and as the interior surface of the tube is left in such a very dirty condition as to obscure the result, we prefer to transfer the tube to a jar of water, which, when the cap is removed, at once displaces the mercury and washes out the interior, without sensibly impairing the accuracy of the experiment.

Water.—The points to be illustrated in the case of water or rather of free steam are all indicated by the equation

$$\boxed{HH} + \boxed{O} = \boxed{H_2O}$$

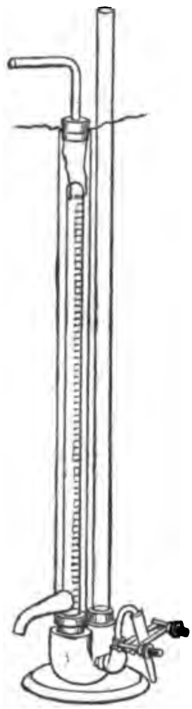
There is no more striking experiment in this connection than the decomposition of water by sodium, but as made in the usual way the experiment is attended with no little danger. Sodium in certain states explodes violently when brought in contact with water, and after several accidents of this sort we have substituted the solid sodium amalgam above described with the best results. We place an ounce or more of this amalgam in a common gas flask and pour upon it water. The action is very moderate and must be assisted by a gentle heat, but on heating the flask with a gas lamp the gas is evolved rapidly and with great regularity. We collect it over the pneumatic trough and illustrate its properties in the usual way.

We illustrate the fact that water is composed of two volumes of hydrogen to every one of oxygen by the electrolysis of dilute sulphuric acid, using for the purpose the decomposing cell, fig. 1, already described. We collect the gases in two tall bell glasses standing side by side on the shelf of the same pneumatic trough. These bells are of course calibrated and the equal divisions marked by rubber rings. Six cells of Bunsen's battery, medium size, give a rapid evolution of gas.

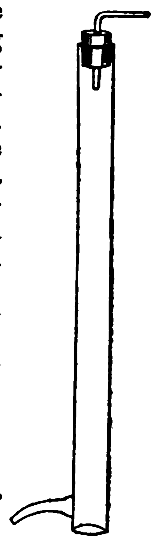
Lastly we illustrate the fact, that when the elementary gases unite to form aqueous vapor, three volumes are condensed to two, by means of the eudiometer represented in fig. 7. This

apparatus is easily made with a common iron casting well known to steam fitters as a "return bend." Any machinist will easily adapt this casting to the required use by attaching to it, as shown in the figure, a circular iron plate to serve as a stand, by also screwing on to one side an ordinary "elbow joint," and at the same time by carefully rimming out the three apertures so as to present smooth surfaces for the adhesion of the rubber stoppers. Into one of the openings of the "return bend" we fasten with a perforated rubber stopper, a common straight *eudiometer tube*, such for example as is ordinarily used in Bunsen's method of gas analysis, while into the second opening we fasten in a similar way an *open* glass tube. In the opening of the elbow joint we secure with a perforated rubber stopper as before, that convenient substitute for a stop cock so well known to chemists as a nipper tap. Last of all we obtain from the glass house a tubulated tube like that shown in fig. 8, of such size that it will cover the eudiometer tube and fit the upper end of the same rubber stopper by which the last is secured in its place. The upper end of this *outer tube* is also closed with a perforated stopper, as shown in the figure, and fine platinum wires, connecting with the wires of the eudiometer, pass between the stopper and the glass. The lower end of the outer tube should not fit too tightly around the rubber stopper so that it can easily be removed when not wanted, moreover all the stoppers should be made of such length that while perfectly tight, they can easily be removed for cleaning the tubes.* These rubber joints, if well made, give great flexibility to the apparatus and enable it to withstand quite rough usage.

7.



8.

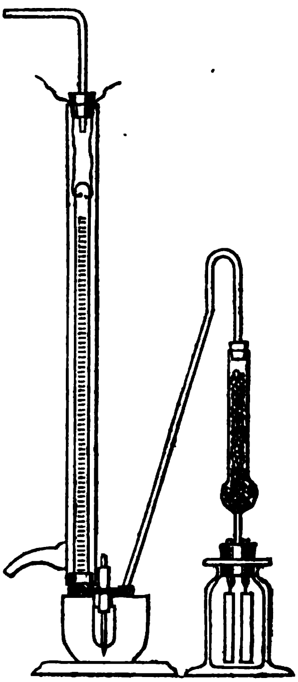


The eudiometer being thus mounted, mercury is first poured into the open limb, which is then closed with a rubber stopper and the mercury transferred by inclining the apparatus to the

* It is also best to place around the upper end of the eudiometer tube a rubber ring, quite narrow, but sufficiently thick to fill the annular space when the outer tube is in its place, and also perforated with a number of small holes, so that the steam or vapor, employed in the experiments, may pass freely. This ring confines the eudiometer tube and gives greater solidity to the apparatus.

closed limb, this process being repeated until the eudiometer tube is full. The excess of mercury is now drawn out of the open tube by the tap and this tube having been removed the instrument is left as represented in fig. 9. The eudiometer is now ready for receiving the mixed gases, which are passed up into it from a simple decomposing cell, as shown in the figure, the excess of mercury overflowing into any convenient vessel. The *open tube* is now replaced and the outer tube secured in position. It is next necessary to raise the temperature of the eudiometer tube to a point considerably above the boiling point of water and maintain it at this temperature during the rest of the experiment. This is most conveniently done by passing through the *outer tube* the vapor of amylic alcohol (fousel oil,) which may be generated in a flask placed at one side and connected by a glass tube with the upper end of the apparatus. The tubulature at the lower end of the tube should at the same time be dipped into the mouth of a glass bottle into which the alcohol may flow as fast as the vapor is condensed, and since the latent heat of this vapor is very small, this simple method of condensation will be found amply sufficient.

9.



As soon as the temperature of the eudiometer tube is constant, which can easily be told, because the mercury column will then remain at a constant height, mercury must be poured into the open tube or withdrawn from it by the nipper tap until the level is the same in both limbs of the apparatus. It remains now only to note the volume of the confined gas and to explode it by passing an electric spark through the platinum wire already noticed, first, however, tightly closing the end of the open tube with its rubber stopper. When the stopper is removed and the mercury columns again brought to the same level it will be found that the volume of the confined gas has been reduced one-third. The result, however, is always a little too small, because aqueous vapor, even at the boiling point of amylic alcohol, 132° C., does not exactly obey Mariotte's law, and is somewhat more condensed than the *mixed gases* by the atmospheric pressure. It would be better to employ the vapor of a liquid having a still

higher boiling point, but the results with amylic alcohol are sufficiently accurate for a lecture experiment.*

Ammonia.—The points to be illustrated in the case of ammonia are indicated by the equation $\boxed{\overbrace{H\ \ H\ \ H}}+\boxed{\overbrace{N}}=\boxed{\overbrace{H_3\,N}}$.

We demonstrate the composition of ammonia by the old methods which are familiar to every teacher, synthetically by passing a mixture of nitric oxyd and hydrogen over heated platinum sponge as in the beautiful experiment of the late Dr. Hare, and analytically by decomposing aqua ammonia either by electrolysis or by means of chlorine. For the electrolysis of ammonia the decomposing cell fig. 1 may be used, filling it with the strongest aqua ammonia and adding a not too small amount of sulphate ammonia in order to increase the conducting power of the liquid. The reaction is less simple than in the electrolysis either of water or of hydrochloric acid, but as the final results the gasses are evolved, very nearly at least, in atomic proportions, three volumes of hydrogen to one of nitrogen. They can be collected separately in graduated bells as in the electrolysis of water. In decomposing ammonia by chlorine we use with very satisfactory results the apparatus shown in fig. 6 and already described. For this use however a tube should be selected so thin that water may be boiled in it without risk of breaking the glass. The tube having been filled by displacement with pure and dry chlorine gas, we press down the lower end into very weak aqua ammonia (eight measures of water to one of the concentrated solution,) until the liquid flowing in through the overflow tube rises to the height of the first rubber ring. We now quickly close the delivery tube with its rubber cap and allow the absorption to continue until the tube is about half full of the ammonia water when we also close the overflow tube and shake up the liquid in the large tube until all cloudiness has disappeared from the interior. The decomposition is now complete but a considerable amount of the liberated nitrogen still remains dissolved in the liquid. To expel this we heat the tube carefully over a gas lamp until the liquid within begins to boil. On now transferring the apparatus to the pneumatic trough and opening the overflow tube under water it will be found, when the tube cools, that just one-third of the original volume is left and it can easily be shown that the residual gas

* Indeed we can obtain with free steam a result, which is sufficiently near the theory for all purposes of illustration, only it is then important that both the mixed gases and the resulting vapor should be measured under a pressure considerably less than that of the atmosphere. For this purpose a long eudiometer tube should be used and before each measurement the level of the mercury should be adjusted so that it shall stand in the open tube from 10 to 15 inches lower than in the eudiometer. Of course the difference of level must be the same at both measurements.

is nitrogen. Hence, it follows, since chlorine always combines with its own volume of hydrogen, that ammonia contains only one volume of nitrogen to every three volumes of hydrogen, the point to be proved. To complete this series of illustrations it only remains to show that in ammonia gas the four volumes are condensed to two. For this purpose some dry ammonia gas is passed up into the eudiometer tube as in fig. 9. The side tube is then replaced as in fig. 7, the mercury level adjusted and the position marked with a rubber ring. A stream of electric sparks from a Rühmkorff coil is now passed through the gas, so arranging the connections that the sparks may traverse the whole length of the gas column, and the amount of gas should be small enough to render this possible. The decomposition proceeds somewhat slowly, but after sufficient time on readjusting the level it will be found that the volume of the gas has doubled. Besides the experiments described above, there are many others, to which these same forms of apparatus are applicable; but these will suggest themselves to every teacher and it is not therefore necessary to enter into further details.

Eudiometer.—The eudiometer described above, although originally contrived for the lecture table has proved to be of still greater value in the laboratory, in all processes of gas analysis for which such an instrument is required. It is not only very cheap, simple, and easily repaired, but also equally as accurate as the the most complicated apparatus. It can be used in a room of the most variable temperature; for by passing a current of water, or of steam, as the case may require, through the outer tube the temperature of the eudiometer tube may be easily maintained absolutely constant. The various gases are passed in as shown in fig. 9 and through the same opening the reagents used in the processes of analysis are readily introduced. By replacing the open tube as in fig. 7, and bringing the two mercury columns to the same level, the residual volumes may always be read off under the atmospheric pressure and at a constant temperature, indicated by a thermometer placed in the annular space between the tubes. Or on the other hand by varying the height of the mercury column in the outer tube we may reduce the gas to the same volume and measure the difference of tension according to the method of Regnault. This form of eudiometer is especially adapted for the admirable methods of gas analysis devised by Bunsen. The absorbent balls used by him are most readily introduced when the apparatus is arranged as shown in fig. 9 and the volume of aqueous vapor formed after combustion may easily be measured by replacing the current of cold water through the *outer tube* by a current of free steam. In this case it will be best to measure the gas under as great a difference of pressure as possible, in order to ensure that all the

water is vaporized and also in order to avoid the somewhat uncertain correction arising from the difference of temperature of the two limbs of the apparatus. This correction, which in most cases is insignificant, becomes important when steam is used, and it is then best to measure directly the difference of level between the mercury in the open mouth of the iron cistern, fig. 9, and that in the tube. This we do by the millimeter divisions on the eudiometer tube with the aid of a very simple contrivance. A split ring of blackened sheet brass, carrying a bent steel wire, is slipped down over the outer tube until the end of the wire just touches the surface of the mercury. The vertical height of this simple measure being known we have only to add to it the height of the mercury column above the upper edge of the ring in order to know the exact difference of level. Of course care must be taken when the measurement is made that the mercury column is vertical, but it is unnecessary to dwell on such obvious precautions, which are essentially the same with this apparatus as those so fully detailed by Bunsen in his work on "Gasometry." It is obvious moreover that the number of these corrections is considerably diminished in using this apparatus as compared with the ordinary mercury pneumatic trough, and besides the convenience and comfort of working in a warm room, it has the additional recomendation that it requires a very small amount of mercury.

The above apparatus as represented in fig. 9 may also be used with great advantage in Gay Lussac's process of determining the density of vapors. The method of using it is obvious to any one who is familiar with the process. After a weighed amount of the liquid under examination enclosed in a thin glass bulb has been passed up into the eudiometer tube it is readily converted into vapor by passing steam or the vapor of some liquid of a still higher boiling point* through the outer tube. All the measurements required in the determination are now easily made. The temperature is measured by a thermometer placed in the annular space between the two tubes and the difference of level of the mercury in the two limbs of the instrument may be most accurately determined by means of a cathetometer aided by the simple contrivance just described.

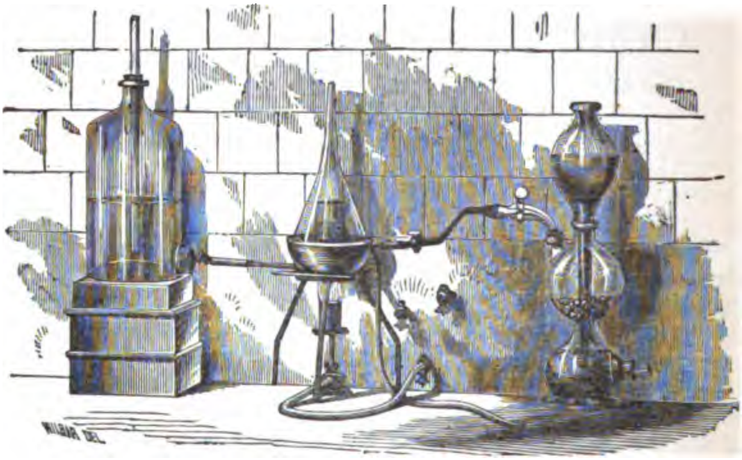
* Hydrocarbons of high but still constant boiling points, obtained by the methods of Mr. C. M. Warren, might be used with proper precautions in such determinations.

II.—A METHOD OF DETERMINING THE AMOUNT OF PROTOXYD OF IRON IN SILICATES NOT SOLUBLE IN THE ORDINARY MINERAL ACIDS.

THE accurate determination of the amounts of protoxyd and sesquioxyd of iron in siliceous minerals is a point of much importance in mineralogy, and when the silicate can be dissolved by the ordinary mineral acids, this determination presents no great difficulties. But it is very different with the so-called insoluble silicates. In regard to these the problem has never been satisfactorily solved; so that the exact condition of oxydation of the iron in some varieties of the most common species is not with certainty known. Many siliceous minerals which are not perfectly decomposed by the dilute mineral acids in an open vessel, are dissolved after long digestion in a sealed flask, and in a former paper the author described a simple and accurate method of determining the amount of protoxyd of iron in all silicates of this class. The method here described applies chiefly to the silicates, which cannot be thus decomposed and is based on the use of hydrofluoric acid as a mineral solvent. With a very few exceptions all silicates are dissolved after a more or less prolonged digestion in a mixture of sulphuric and hydrofluoric acids, and in this solution the amount of protoxyd of iron can be accurately determined with permanganate of potassa. It is of course essential that the solution should be made out of contact with the air and the difficulty of fulfilling this condition with hydrofluoric acid has probably been the reason why this valuable reagent has not been hitherto used in iron determinations. This difficulty however may be completely overcome by the apparatus represented in the accompanying figure which, although it may appear complicated at first sight, is really a simple combination of parts, which are familiar in every laboratory.

To the sides of a common copper water bath are attached three tubes as is shown in the figure. The tube on the left connects with a Mariotte's flask by which the water is maintained at a constant level in the bath. The upper tube on the right connects with a carbonic acid gas generator, while the lower tube (connected with the sink by a rubber hose), serves simply

as an overflow for the water. On the cover of the water-bath close to the rim is a depressed circular groove, which receives the lip of an inverted glass tunnel. When the apparatus is in



use this groove is kept full of water by the spray from the boiling liquid and thus forms a perfect water joint; but in order to secure this result the bath must be kept nearly full of water and holes for the ready escape of the steam and spray should be provided in the copper rings, which cover the bath and adapt it for vessels of various sizes. It is evident that, by this simple modification of the ordinary water-bath, we can keep our assay surrounded by an atmosphere of steam or of carbonic acid, as may be desirable, during the whole process of digestion, and that too for an indefinite period. Moreover while watching the process through the glass we can either pour in fresh quantities of the solvent, or we can stir up the material, in the vessel within, introducing a tube-tunnel or stirrer through the spout of the covering tunnel.

After the above description the method of making the iron assay will be readily understood. A small amount of the finely pulverized mineral (from one-half a gram to a gram) is weighed out in a large platinum crucible. Upon this we pour a mixture of dilute sulphuric acid (sp. gr. 1·5) with as little hydrofluoric acid as experience may show is required to dissolve* the mineral stirring up the material with a platinum spatula. The crucible is next transferred to the water bath, the covering tunnel put in place, water poured into the groove, the interior filled with car-

* If the mineral contains lead, baryta, strontia or even lime in any considerable quantity, complete solution cannot of course be obtained, but this is unimportant so long as the mineral is wholly decomposed.

bonic acid from the generator and the gas lamp lighted. As soon as the water boils, the connection with the generator is closed, and if the water level has been properly adjusted, the apparatus will take care of itself, the groove will be kept full of water and the interior of the tunnel full of steam. If the materials cake on the bottom of the crucible,—as is not unfrequently the case when a large amount of insoluble sulphate is formed,—the lamp may be removed, the apparatus again filled with carbonic acid, and the contents of the crucible stirred up as above described. A stout platinum wire about two inches long, cemented before the blow-pipe to the end of a glass tube, makes an excellent stirring rod, and after using it any adhering material can easily be washed back into the crucible by directing the jet from the wash bottle down the throat of the covering tunnel. The lamp may then be replaced, the current of carbonic acid interrupted and the process of digestion continued. When the decomposition is complete the current of carbonic acid gas is reëstablished, the lamp extinguished and the air tube of the Mariotte's flask raised until its lower end is above the level of the overflow. A slow current of water is thus caused to flow through the bath, which soon cools down the whole apparatus. The crucible, may now be removed, its contents washed into a beaker glass and the solution diluted with pure water until the volume is about 500 $\overline{\text{c.m.}}^3$, when the amount of protoxyd of iron present can be determined with a solution of permanganate of potassa in the usual way. The total amount of iron present being subsequently determined, the relative proportion of the two oxyds is of course well known. In order to show the accuracy of the method and also to prove that the presence of hydrofluoric acid does not exert any appreciable influence on the permanganate solution we subjoin the following results.

The strength of the solution of permanganate was tested with the double sulphate of ammonia and iron. In each case 1·4 grams of the salt were accurately weighed out and dissolved in about 500 $\overline{\text{c.m.}}^3$ of water. To the first two portions sulphuric acid was alone added while to the last two there was also added a very large amount of hydrofluoric acid, four or five times as much as would be required in any mineral analysis. The results were

No. 1,	1·4	grams	iron	salt	required	26·35	$\overline{\text{c. m.}}^3$	permanganate.
No. 2,	"	"	"	"	"	26·35	"	"
No. 3,	"	"	"	"	"	26·4	"	"
No. 4,	"	"	"	"	"	26·45	"	"

From a specimen of very dark green actinolite treated as above described we obtained in three determinations the following results.

No. 1,	0·6913 grams	of mineral	required	14·1	$\overline{c.m.}^3$	permanganate.
No. 2,	0·6640	"	"	"	13·6	"	"
No. 3,	0·8910	"	"	"	18·2	"	"

The per centage composition deduced from this is

	Per cent of FeO.
No. 1,	19·86.
No. 2,	19·95.
No. 3,	19·89.

In order to test still further the efficiency of our apparatus we have several times dissolved 2 decigrams of iron in dilute sulphuric acid and heated the solution in the bath for more than twelve hours without its undergoing the slightest oxydation.

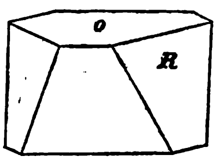
It is of course essential in this process that both the sulphuric and hydrofluoric acids should be perfectly pure and wholly free from any oxydizing or reducing agents. There is no difficulty in obtaining from the manufacturers pure sulphuric acid, but unfortunately the commercial hydrofluoric acid is apt to be very impure and must be carefully purified by repeated distillation before it is used in this process. The apparatus here described will also be found very useful in the ordinary iron assays and is also applicable in a large number of analytical processes, where it is necessary that the assay should not be exposed to the air. Of course in such cases a glass beaker would take the place of the platinum crucible, as is shown in the figure. Lastly, this method of heating in an atmosphere of steam will be found very convenient in the many cases where it it is desirable to prevent the evaporation of water during the process. The presence of the steam moreover, prevents to a great degree the escape of the volatile acids; so that in the process above described, the glass covering tunnel is not perceptibly corroded unless the hydrofluoric acid used is very strong.

Cambridge, June 22d, 1867.

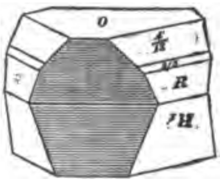
III.—CRYSTALLOGRAPHIC EXAMINATION OF SOME AMERICAN CHLORITES.

THROUGH the kindness of my friend Prof. Brush of New Haven, I have had the opportunity of examining some unique specimens of the Chlorites from the well known locality at Texas, Lancaster county, Pennsylvania. My observations confirm in almost every particular, those previously made by M. Des Cloizeaux and published in his admirable Manuel de Mineralogie, tome i, pp. 433–451; but the perfection of the crystals at my disposal have enabled me to obtain a greater degree of accuracy in my measurements and also to develop some additional facts, especially by comparing the clinochlore from Texas, Pennsylvania, with that from Chester county in the same state and also with that from Chester in Massachusetts.

1.



2.



Kämmererite or Violet Chrome Chlorite.—The purest crystals of this beautiful mineral have the form represented in fig. 1. They are generally, however, macled and then appear as in fig. 2. Besides the basal plane O and the planes of fundamental rhombohedron R, these crystals also present the planes of several subordinate rhombohedrons of somewhat variable character, and in addition the basal edges of the rhombohedrons are more or less modified by the planes of hexagonal pyramids, but unfortunately the last are so strongly striated and uneven as to be wholly indeterminable. The violet Kämmererite is frequently mixed with green clinochlore, which gives to the crystals a greenish tinge. On these compound crystals the pyramidal planes are much more dominant than on the crystals of pure Kämmererite, and in this way the crystals of one mineral pass into those of the other, the violet rhombohedrons of Kämmererite merging into the green hexagonal pyramids of clinochlore. We give below in column A, the results of measurements of by far the most perfect crystal of Kämmererite we have examined. The angles italicised are certainly accurate to a minute. In columns B_1 and B_2 we give angles measured on two separate zones of a second crystal and these are important as proving the hexagonal character of the crystal. In column C, we give the fundamental angle measured on still a third crystal. The last two crystals were not so perfect as the first, but still the angles italicised must have been measured accurately within two or three minutes; so that

the small differences between these values and those in column A are real variations in the angle, such as are quite common in foliated minerals. All the crystals measured were macled as in fig. 2, and we have distinguished the faces of the two members of the macle by the symbol O, R, etc., for the first, and O_1 and R_1 for the second. It is a fact worthy of notice that the faces of the same subordinate rhombohedrons are not necessarily found on both of the twinned crystals, while those of the fundamental rhombohedron are never wanting. On the first crystal we were able to measure every angle of the zone of planes between the opposite basal planes of the macle, and the observations were verified by repeated measurements. It will be noticed that the corresponding angles on the two crystals composing the macle agree absolutely. From these I have calculated the value of the half vertical axis, and from the last I have deduced the values of the angles in the column headed calculated.

$a = 3{\cdot}4951$

	Calculated.	Observed. A	B_1	B_2	C
O on R	103° 55′	**103° 55′**		**103° 41′**	**103° 41′**
O on $\frac{4}{13}$R	128° 51′	128° 59′	**129° 6′**	**129° 8′**	•
O on $\frac{2}{5}$R	121° 47′	121° 54′		122° (nearly)	
$\frac{4}{13}$R on $\frac{2}{5}$R	172° 56′	172° 55′			
$\frac{2}{5}$R on R	162° 8′	161° 59′			
R on R_1	152° 10′	**152° 10′**			
R_1 on O_1	103° 55′	**103° 55′**			
O_1 on O_1	180°	**180°**			
R on R (vertical edge)	65° 36′				

Des Cloizeaux obtained from the same mineral O on R 103° 45′, O on $\frac{2}{5}$R, 122° (about), and from the Pennine of Zermatt for O on R 103° 40′ to 50′.

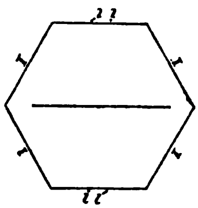
Optical characters of Kämmererite.—The crystals are *uniaxial*, and the double refraction though *feeble* is distinctly *positive*. The crystals described above as No. 1, showed distinctly the first two rings with the familiar black cross. In white light these rings are alternately blue and pink surrounding a pink-colored center. In homogeneous light the rings formed by the red rays are much narrower than those formed by the blue, indicating the somewhat unusual fact that the crystal exerts the feeblest dispersive power, on the most refracted, in this case the extraordinary, beam. The crystals of Kämmererite are strongly dichroic. By transmitted light in the direction of the optical axis the color is violet; but in all directions at right angles to this, while the color of the ordinary beam is violet, that of the extraordinary is hyacinth-red. Before the blowpipe the mineral gives decided reactions both for chromium and iron.

Pale Green Chlorite.—Accompanying the specimens of Kämmererite I received a single specimen of another variety of Chlo-

rite having a very pale apple-green color. It came from the same locality, but how closely it is associated with the violet mineral, I have not as yet been able to ascertain. The crystals are six-sided plates with an angle of 120° between the lateral edges, and the edges are beveled by the planes of a very acute hexagonal pyramid. With the exception of the color, and the strong dichroism, which is in a measure the result of the color, the optical qualities are essentially the same as those of Kämmererite. The crystals are uniaxial and they present the same *feeble*, *positive* double refraction. Moreover the rings formed by red light are narrower than those formed by blue light. Before the blowpipe the mineral gives a decided reaction for iron; but only a very faint reaction if any for chromium, and the difference of color is evidently connected with this difference of composition.

Clinochlore from Texas.—Intimately associated and more or less mixed with Kämmererite are crystals of clinochlore which in their purest condition have a brilliant emerald-green color. These crystals of pure clinochlore are double hexagonal pyramids, but the faces of the pyramids, are so irregular and strongly striated that it is impossible to determine the crystallographic elements of the crystals. The crystals cleave easily parallel to the basal plane and they may thus be readily divided into hexagonal plates with an angle of 120° between the lateral edges. These plates show a strong double refraction and the plane of the optical axes is parallel to the edge of the hexagonal section as shown in fig. 3. The bisectrix of the acute angle between the optical axes is positive, and inclined at a variable angle to the normal of the plane of cleavage. The angle between the optical axes is also exceedingly variable. The following angles were measured on cleavage plates from different crystals. These are not of course the true angles; but the great fluctuations of the value makes any reduction of the observations unimportant.

3.



	Apparent angle between optical axes.	Apparent angle between bisectrix and normal.
No. 1,	84°	15° 30′
No. 2,	79°	
No. 3,	67°	13° 30′

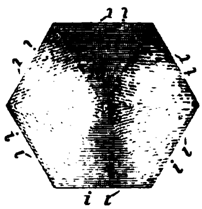
The dispersion of the axes is quite evident, and in every case $\varrho > v$. Moreover, the system of rings, when seen by white light, shows a slight but distinct difference of form at the two ends, thus indicating that the general dispersion of the system is longitudinal;* and this characteristic further indicates that the crys-

* The modifications in the biaxial system of rings called by Des Cloizeaux "dispersion inclinée," "dispersion horizontale" and "dispersion croisée ou tournante" we

tals belong to the monoclinic system, and that the optical axes are in the plane of symmetry. These crystals of clinochlore also show a marked dichroism. The color by transmitted light in the direction of the optical axis is emerald green but in all directions at right angles to the axis, while the color of the ordinary beam is green, that of the extraordinary is reddish yellow.

The crystals of clinochlore from Texas are almost invariably macled. The ideal macle, if I may use the term, consists of three crystals interpenetrating each other, as is shown in section in fig. 4 where the portions of different crystals are distinguished by the shading, the lines of the shading indicating also the position of the plane of the optical axes. It is seldom the case, however, if ever, that the macles have the regularity, which our figure would indicate, although I have frequently observed on different parts of the same plate three different systems of rings, the planes of whose axes make angles of 60° with each other. In an intermediate position a complex form would be seen resulting from the overlapping and interfering of the three systems. Generally, however, the crystals are united in very unequal proportions, some one or two being present in very great excess and giving rise to corresponding irregularities in the figures seen by polarized light. With many plates the combined figure just spoken of would alone be seen, while with others you would see over most of the plate only one ring system, a single corner perhaps showing evidence of macling. When, as is frequently the case, the crystals of clinochlore enclose those of Kämmererite the result is still more complex. At times the crystal of Kämmererite forms the nucleus of a larger crystal of clinochlore, while in other cases these two heteromorphous minerals seem actually to interpenetrate each other; and in all cases the cleavage planes of the two crystals absolutely coincide. The crystals of clinochlore thus acquire *a violet tinge* and at the same time the angle between the optical axes is diminished. Moreover we have observed on such crystals a character not unlike that first noticed by De Senarmont on certain artificial crystals and to which he referred the variation in the angle of the optical axes of the micas. Thus on moving a plate of violet tinged clinochlore parallel to itself in front of the polarizing microscope I found that the angle between the optical axis varied as I passed from one side of the field to the other. The successive values which

4.

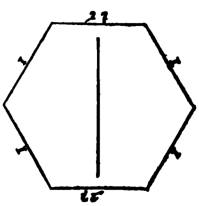


have named in English longitudinal, lateral and circular dispersion. The English terms are not the exact equivalents of the French words, but they express the idea that the effect of light of different colors is, in the first case to move the system of rings longitudinally, in the second case to move it laterally, and in the third case to revolve it through a small angle around the bisectrix.

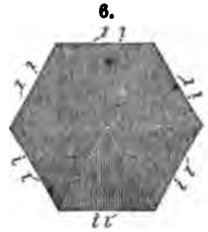
I obtained were 27°, 26°, 19° 30′, 18°, 17°, 16°. On another plate beginning with an angle of 30° I next measured an angle of 18°. Moving the plate still farther, always parallel to itself, the axes closed together and then again opened as I passed on to another portion of the macle. It will be noticed that the largest of these angles is much smaller than those observed on crystals of pure clinochlore, and on placing a plate of pure Kämmererite behind a plate of pure clinochlore I observed not only that the angle between the optical axes was diminished but also that the color of the light transmitted through the two plates was precisely the same as that seen through plates of the compound crystals we have been discussing.

Clinochlore from Chester county, Pennsylvania.—In connection with the clinochlore from the Chrome Iron Mines of Texas, Pa., I have reëxamined that from the serpentine of West Chester in the same state. As is well known these large crystals are so exceedingly irregular that the form cannot be accurately determined. Like other crystals of chlorite, they have an easy micaceous cleavage, and the cleavage section is either hexagonal or triangular, the angle between the adjacent edges of the section measuring 120° or 60° as the case may be. The optical characters are in most respects the same as those of the corresponding mineral from Texas. There is the same strong double refraction and biaxial character, the same inclination of the bisectrix to the plane of cleavage, the same variation in the angle between the optical axes, the same system of macles, the same color and the same dichroism; but still there is one important exception. The line uniting the centers of the biaxial image is not parallel but perpendicular to the edge of the hexagonal section as is shown in fig. 5. This fact first observed by Mr. W. P. Blake I have verified on a number of different plates, and I have not been able to find a single exception to the rule. Moreover, this position of the plane of the optical axes is preserved in the macles. An ideal section of such a macle is represented in fig. 6, where as in fig. 4 the position of the plane of the optical axes on different parts of the plate is indicated by the lines of the shading; and in some plates this ideal arrangement is very nearly preserved, although generally we find the same irregularities already noticed on the macles from Texas. Lastly, the dispersion is not *longitudinal* but *lateral*. This dispersion of the biaxial image is so slight, however, that it might be readily overlooked. It is manifested only by a slight difference in the curvature of the rings and in the

5.



6.



intensity of their color on the two sides of the image, but then this difference is constant and after examining a large number of plates placed in different positions in the field of the microscope I was left in no doubt as to the fact. It follows then, that while these crystals are monoclinic and the position of the bisectrix is the same as in the crystals from Texas, the plane of the optical axes instead of coinciding with the plane of symmetry is at right angles to this plane.

Clinochlore from Chester, Massachusetts.—Through the kindness of Dr. C. T. Jackson of Boston I have had the opportunity of examining some well-characterized chlorite crystals, which occur at the emery mine of Chester, Mass., in connection with diaspore and its associated minerals. The crystals are double hexagonal pyramids but very rough and irregular. They have a micaceous cleavage yielding an hexagonal section, and the angle between the adjacent edges of the section measured on two different plates exactly 120°. The optical characters are all those of clinochlore; strong double refraction; biaxial image with the bisectrix inclined to the cleavage plane; and moderate dispersion of the axes $\rho > \upsilon$. Moreover the angle between the optical axes is very variable. I measured on different cleavage plates, all from this one locality, the angles 73° 30′, 71° 30′, 45°, 32°. The line joining the centers of the biaxial image is perpendicular to the edge of the hexagonal section, and the dispersion of the image is lateral as in the crystals from Chester Co., Pa. Indeed these crystals resemble the last in almost every respect except that they are smaller, have a deeper color, and are not so generally macled.

Analogies between the Chlorites and Micas.—Although these two minerals crystallize in very different systems, yet the analogies between their crystalline characters is very remarkable. In crystals of both minerals the section made by the cleavage plane is a regular hexagon; in both, the double refraction is strong and the angle between the optical axes is very variable; in both we can distinguish two optically distinct varieties, in one of which the plane of the optical axes has the position shown in fig. 3, while in the other it has the position shown in fig. 5. Lastly Kämmererite and Pennine stand in somewhat the same relation to the two varieties of clinochlore that Vesuvian Biotite stands to the two corresponding varieties of mica, although it must be remembered, that while the double refraction of the uniaxial chlorite is very feeble that of the uniaxial mica is still quite strong. Mineralogists generally admit with DeSenarmont that the variations in the optical axes of the micas result from the mutual influence of the two optical varieties and the facts of this paper tend to show that the same influence is exerted on the chlorites.

Cambridge, June 29th, 1867.

[FROM THE AMERICAN JOURN. OF SCIENCE AND ARTS, VOL. XLII, JULY, 1866.]

ON DANALITE,

A NEW MINERAL SPECIES FROM THE GRANITE OF ROCKPORT, MASS.

BY JOSIAH P. COOKE, JR.

DISSEMINATED through the Rockport granite, which is quarried at the extremity of Cape Ann, Massachusetts, and much used for building in Boston and the vicinity, are occasional grains of a flesh-red mineral somewhat resembling Rhodonite.

The mineral has been at times found in masses of considerable size, and for a specimen of this sort I am indebted to the kindness of Mr. W. J. Knowlton, of the Lawrence Scientific School.

The characters of the mineral are as follows: Color, flesh-red to gray. Streak similar in color to the mineral but lighter. Lustre, vitreo-resinous. Translucent. Fracture subconchoidal uneven. Brittle. Hardness 5·5 to 6. Specific gravity—two determinations—3·427. The exterior portion of the mass showed no indication of crystalline form and there was no distinct cleavage; but on breaking it open a well developed octahedron of the regular system was found in the interior. The angle between the octahedral faces measured with an application goniometer 109° 30′. The edges of the octahedron were replaced by planes of a rhombic dodecahedron, strongly striated parallel to the longer diagonal of the face. The mineral, therefore, crystallizes in the *holohedral* forms of the monometric system.

Before the blowpipe the mineral readily fuses on the edges to a black enamel. Hence its fusibility is about 4 of von Kobell's scale. On charcoal with carbonate of soda it gives a slight coating of oxyd of zinc. In a closed tube it loses color, but gives off no water or any sublimate. It is perfectly decomposed after some time by hydrochloric acid, the silica partly gelatinizing. It is also decomposed by nitric acid; but then the silica separates as a powder. It is partially decomposed by dilute sulphuric acid, and even by acetic acid, sulphid of hydrogen gas being evolved.

In order to thoroughly decompose the mineral the material was finely pulverized and sealed up with some concentrated acid in a glass flask, which was then exposed for several hours to the heat of a water-bath. When hydrochloric acid was used a slightly greenish solution was obtained, frequently depositing crystals of protochlorid of iron on cooling, but showing no traces of sesquichlorid, and on opening the flask a strong odor of sulphid of hydrogen was observed. When nitric acid was used the flask became filled with nitrous vapors, and both the

iron and the sulphur were completely oxydized. A qualitative analysis proved the mineral to be a compound of silica, glucina, protoxyd of iron, oxyd of manganese, and oxyd of zinc, mixed with the sulphids of the last three metals. The presence of alumina could not with certainty be detected by any known tests. The precipitate of glucina perfectly redissolved in an excess of carbonate of ammonia, and no crystals of alum could be obtained from a solution of the sulphate when treated in the usual way with an excess of sulphate of potash, although they were sought for with a microscope.

As the sulphid of hydrogen which is evolved from the metallic sulphids, when the mineral is decomposed by hydrochloric acid in a closed flask, would necessarily reduce all the iron present to the condition of proto-chlorid, the following experiment was made to determine the original condition of the iron in the mineral. It is evident that any such reduction must be attended with the separation of free sulphur, and hence sulphur was sought for in the products remaining in the flask after the decomposition was finished. The sulphid of hydrogen and the greater part of the free hydrochloric acid having been first expelled, the residue was boiled with an excess of concentrated nitric acid, and as no trace of sulphuric acid was found it was concluded that the iron in the mineral, not united with sulphur, was all in the condition of protoxyd. The same experiment also proved that none of the varieties of iron pyrites could be present in the mineral in distinct grains, as was at first suspected; and this conclusion was confirmed by the fact that a powerful magnet failed to attract any portion of the mineral, even when reduced to the finest powder.

In the quantitative analysis no unusual methods were employed. The mineral was decomposed in a sealed flask as described above, sometimes by hydrochloric but usually by concentrated nitric acid. The silica was separated in the ordinary way and its purity tested by hydrofluoric acid, the small amount of residue, which was in some cases obtained, being carefully determined and estimated in calculating the final result. The iron was then precipitated as basic acetate, and this precipitate carried down with it a portion of the glucina. From the filtrate the manganese was separated by bromine, and the zinc was precipitated by sulphid of hydrogen. The filtrate from the sulphid of zinc was always found to contain the larger part of the glucina,[1] which was precipitated by ammonia. The glucina thus precipitated was weighed down by itself and the amount added to that subsequently separated from the iron. This last

[1] We have never succeeded in precipitating the whole of the glucina as basic acetate, although carefully attending to all the precautions which have been indicated by other analysts. But alumina is perfectly precipitated when the necessary precautions are observed.

separation was effected by a simple modification of Deville's method which will be described at the end of this article. Lastly, the sulphur, which now remained in solution as sulphuric acid, was determined as sulphate of baryta in the usual way. The results of my analyses were as follows:

	1.	2.	3.	4.	Mean.
Silica,	31·74	31·54	31·96	31·69	31·73
Protoxyd of iron,	....	....	25·71	29·09	27·40
Oxyd of zinc,	17·90	16·90	19·11	16·14	17·51
Oxyd of manganese,	5·83	6·64	6·17	6·47	6·28
Glucina,	....	....	13·86	13·79	13·83
Sulphur,	....	....	5·93	5·02	5·48
			102·74	102·20	102·23
Oxygen equivalent to per cent of sulphur,			2·96	2·51	2·74
			99·78	99·69	99·49

For analysis 4 the material used was a portion of the crystal described above. When in mass it had a bright flesh-red color, and even in the powder the color was still quite decided. The material used in analysis 3 was taken from a wholly different portion of the specimen. The red tint was less marked and the color of the powder was decidedly gray. These two portions were selected as presenting the most decided contrasts of color observed. Analyses 1 and 2 were made before the composition of the mineral was correctly known, and the best method of analysis discovered. Hence, only a portion of the bases were accurately determined, and only those results are given which are known to be trustworthy. The material for all the analyses was selected with great care; but that used in 4 being a portion of a crystal from the center of a large mass was unquestionably the most pure.

The most natural theory of the constitution of the mineral, to which the above results and the crystalline form both point, is that the mineral is an isomorphous mixture of a monometric silicate with the simple sulphids of iron, zinc, and perhaps of manganese, all of which affect the same crystalline form. These different sulphids must be present in somewhat varying proportions; for while in 4 the sulphid of iron is evidently in excess, the sulphid of zinc equally predominates in 3, and such a difference is plainly indicated by the difference of color already mentioned. This view is also sustained by the action of different acids on the pulverized mineral. Dilute sulphuric acid attacks the powder even when cold, sulphid of hydrogen being evolved, while iron and zinc in large quantities, with some glucina, enter into solution. Even dilute acetic acid causes an evolution of sulphid of hydrogen dissolving an abundance of iron, but also some glucina. Since now sulphid of zinc is insoluble in acetic acid this last reaction points clearly to the presence of sulphid

of iron in the mineral; but at the same time both experiments indicate that the metallic sulphids are so intimately associated with the silicate that the decomposition of the first involves to a limited extent at least the breaking up of the last. This is what we should naturally expect in an isomorphous mixture, the sulphids not being present in separable grains; but diffused through the mineral in a state of imperfect chemical combination, and thus rendering even a firm silicate exceedingly susceptible of decomposition.

On examining the results of analysis given above it will further appear, in support of the same theory of the constitution of the mineral, that while the proportions of silica, glucina, and even of oxyd of manganese, are very constant, the proportions of the oxyds of zinc and iron vary very considerably; these metals, although in the analyses separated and determined as oxyds, being, in fact, combined to a greater or less extent with sulphur in the different portions of the mass examined. If now we calculate on this view the oxygen ratio of the silicate, deducting of course from the sum of the oxygen of the bases, an amount of oxygen equivalent in each case to the per cent of sulphur found, it appears, taking the mean result, that the sum of the oxygen of the bases is to the sum of the oxygen of the silica as 16·93 : 16·81, or very nearly as 1 : 1. Moreover, if we regard glucina as a sesquioxyd base we shall have for the oxygen ratio between protoxyds, sesquioxyds and silica, the proportion 8·22 : 8·71 : 16·81 or very nearly as 1 : 1 : 2. Again, the amount of sulphur in the metallic sulphids is very nearly one-sixth of the amount of oxygen in the silicate; so that for every twelve equivalents of oxygen in the silicate we have one equivalent of sulphur in the sulphids. Hence we deduce as the general formula of the mineral

$$(\tfrac{1}{2}\dot{R}_3 . \tfrac{1}{2}\ddot{\bar{B}}e)\ddot{\bar{S}}i + \tfrac{1}{2}RS \text{ in which } R = Fe . Zn . Mn.$$

The oxygen ratio of the new mineral is the type ratio of the garnet family, and to this family it undoubtedly belongs. Its minieralógical characters would place it intermediate between Willemite and Iron Garnet where by its composition it naturally falls. This relationship appears in the following table; but it is seen much more clearly on comparing the actual specimens :

	Willemite.	Danalite.	Iron Garnet.
Action of hydrochloric acid,	Gelatinizes easily.	Gelatinizes, but less easily and perfectly.	Decomposed, but does not gelatinize.
Before blowpipe,	Fuses on edges to white enamel.	Fuses more readily to black enamel.	Fuses easily to a bead.
Sp. gr.,	3·39 to 4.	3·427.	3·7 to 4·2.
Hardness,	5·5	5·5 to 6.	6·5 to 7·5.
Luster,	Vitreo-resinous, weak.	ditto, stronger.	ditto, brilliant.

It is true that Willemite and Garnet belong to different crystalline systems, but the ordinary form of Willemite really approaches very nearly a rhombic dodecahedron, the difference of angle only amounting to 5°, and there is no good reason for attaching a greater significance to this difference of angle between the corresponding forms of allied systems, than is attached to an equal difference between similar forms of the same system. In its peculiar constitution the new mineral is allied to Helvin, although the two species have no outward resemblance. The holohedral character of its crystallization, the very large amount of iron and zinc entering into its composition, its color, luster, hardness, and other physical as well as chemical properties, all distinguish it from Helvin and prove the mineral to be a new species. As such I take great pleasure in giving to it the name of *Danalite*, after Prof. James D. Dana, of New Haven, a name so honorably associated with American mineralogy.

Small fragments of Danalite are not unfrequently met with in the quarries at Rockport, and small grains of it, as I have already said, are quite generally disseminated through the granite ledges which form the extremity of Cape Ann. But large masses of the mineral have not been obtained for some time, the portion of the rock in which they were found having been long since quarried. The mineral was first supposed by the local collectors to be Rhodonite, and under this name good specimens of Danalite may probably be found in some of the collections of the country. Specimens of the mineral have also been found associated with green feldspar at the railroad cut near Gloucester, Mass. The mineral at this locality is more garnet-like in structure, and contains a considerable amount of alumina associated with the glucina. An analysis of a specimen from this locality gave the following results:

Silica,	29·88
Protoxyd of iron,	28·13
Oxyd of zinc,	18·15
Oxyd of manganese,	5·71
Glucina and alumina,	14·72
Lime,	0·83
Magnesia,	traces
Sulphur,	4·82
	102·24
Oxygen equiv. to sulphur,	2·41
	99·83

At Gloucester the Danalite is associated with fluor spar, which I have never recognized on the specimens from Rockport, although the granite, in which the mineral is imbedded, has at both localities a similar character. Danalite is also associated at both localities with two very remarkable varieties of lepidolite mica.

These have also been analyzed and an account of the investigation will be given in a future paper.

Separation of Sesquioxyd of Iron from Alumina, Glucina, and most of the rare earths.—The method of Mr. H. Sainte-Claire Deville,[1] referred to in the above paper, is one of the most accurate processes of analytical chemistry, and would probably have been more generally used had it not been supposed that it required a furnace heat and involved the usual accompaniments of furnace work. The simple modification we have introduced is to substitute a tube of platinum for the tube of porcelain, and a Bunsen's blast lamp for the furnace. We use in the process the condenser of a small platinum still; but a smaller tube about 6″ long and $\frac{4}{16}$″ in diameter would be better adapted to the purpose, and would serve many other useful ends in the laboratory. In addition to the tube, a small platinum nacelle would be required, as large as the tube will admit and about $1\frac{1}{2}$″ in length. With such an apparatus the method of conducting the process is as follows: The tube having been mounted horizontally on any convenient stand, one end of it, which is closed by a doubly pierced india rubber cork, is connected on one side with a small hydrogen generator and on the other with a small flask for generating hydrochloric acid gas. To the other end of the tube is fastened by an india rubber connector a small glass adapter, so curved that the end may dip under water. The mixed bases, whose total weight is known, having been placed in the nacelle in a finely pulverized condition, and the nacelle having been introduced into the tube, the heat of a single Bunsen burner is applied, while a gentle current of hydrogen is caused to flow through the apparatus. In the course of half an hour all the oxyd of iron is reduced to the metallic state. The current of hydrogen is then replaced by a much more rapid current of hydrochloric acid gas and the heat of a blast lamp applied. The reduced iron is now rapidly converted into chlorid, which, being volatilized by the heat and carried forward by the current, dissolves in the water. After a few minutes the action ceases, the heat is then withdrawn, and the current of hydrochloric acid gas being again replaced by a current of hydrogen, the apparatus is allowed to cool. The alumina, or whatever earth may be present, is left behind in the nacelle in a perfectly pure condition and can be at once weighed, while the weight of sesquioxyd of iron is known from the loss. If the product is not perfectly white the nacelle should be returned to the tube and the process repeated. The result can be controlled by also weighing the nacelle after the reduction of the iron, but it is not safe to estimate the amount of iron solely from the loss of

[1] Annales de Chimie et de Physique, Tome xxxviii.

weight at this time, since a very small error in this determination would cause an important error in the calculated amount of sesquioxyd. We give these details not as new, but because we feel assured that with the simple modification here described the process will be found far more expeditious, convenient and satisfactory, than any other process now in use. A small porcelain tube might be used instead of the tube platinum, but this cannot be recommended, as the porcelain is liable to break unless protected, and when properly protected sufficient heat can hardly be obtained without a furnace. The hydrogen gas is best obtained from a small automatic generator, and the hydrochloric acid gas may be generated in a small flask from coarse salt and sulphuric acid, which has been previously diluted with about one-third of its volume of water, and allowed to cool. This mixture when gently heated gives a constant flow of gas, which almost immediately stops when the lamp is withdrawn. Both gases should pass through a wash bottle containing strong sulphuric acid before entering the tube.

PROF. J. P. COOKE

ON CRYOPHYLLITE.

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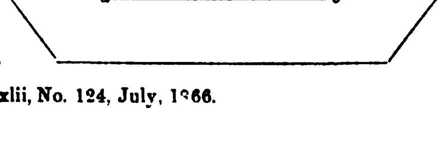
ON CRYOPHYLLITE,

a new mineral species of the Mica Family, with some associated minerals in the granite of Rockport, Massachusetts.

BY JOSIAH P. COOKE, Jr.

In a paper published in a recent number of this Journal* I described a new mineral species allied to Helvin, to which I gave the name of Danalite. Associated with Danalite in the granite ledges forming the extremity of Cape Ann, Massachusetts, are two remarkable micas, one of which is the new species to which on account of its easy fusibility and foliated structure I have given the name Cryophyllite.

Mineralogical Characters.—The mineralogical characters of cryophyllite are as follows. Like other varieties of mica it crystallizes in six-sided prisms, which are frequently of considerable size, from one to two inches in length and of proportionate diameter. The basal cleavage is highly perfect, yielding thin flexible and transparent laminæ, which when examined with a polarizing microscope give a biaxial image, the angle between the optical axes varying from 55° to 60°. The angles 55°, 57° 30′, and 60°, were all measured on different specimens. The dispersion of the axes, if any, is so slight that its character could not with certainty be determined, the color of the mineral tending to obscure any such effect. The perfect uniformity of the two systems of rings both as to form and to color indicates that the mica belongs to the trimetric system. Nevertheless, the angle between the prismatic planes measured with an application goniometer 120° as accurately as is possible with this instrument, and in one instance the planes of an hexagonal pyramid terminating the prism were distinctly seen. Considering, however, these crystals as belonging to the trimetric system, in accordance with the generally received opinion of mineralogists as to crystals of the mica family, all of which present essentially the same crystallographic characters, we must regard the six-sided prism of cryophyllite as formed by the union of the planes *I* of the rhombic prism with the brachydiagonal basal planes *ĭĭ*. The plane of the optical axes coincides with the shorter diagonal of the rhomb base, and the crystals are frequently much elongated in this direction, so that the form of the cleavage face was as shown in the accompanying figure, the line *a b* indicating the position of the plane of the optical axes. Furthermore, the crystals were frequently twinned together



* Vol. xlii, No. 124, July, 1866.

on the plane $i\bar{i}$, and it was observed that in such cases the planes of cleavage of the two crystals were absolutely coincident, proving that the rhombic prisms are rectangular and not oblique, as De Senarmont has previously shown to be true of other crystals of the mica family.

The color of cryophyllite in axial directions is dull emerald green, not unlike glass colored with protoxyd of iron, and so deep that the laminæ are opaque unless quite thin, but like other colored micas it is dichrous and appears brownish-red in the direction of the lateral axes. The color of the streak is light gray with a tint of green. The luster is brilliant on the cleavage face inclining to resinous. The hardness is from 2 to 2·5 and the specific gravity 2·909.

Before the blowpipe cryophyllite very easily fuses with some intumescence to a greyish enamel bead, and it even fuses in flakes of considerable size in the flame of a candle, so that its fusibility is from 1·5 to 2 of von Kobell's scale. It imparts to the flame of a Bunsen's lamp a most brilliant lithia reaction, and by examining the colored flame with a spectroscope the presence of potassium, sodium and rubidium may also be readily discovered. The amount of sodium however must be exceedingly small as it does not sensibly modify the lithia flame as seen by the naked eye, and the same is true to a still greater degree of rubidium. The presence of rubidium is best recognized by mixing the pulverized mineral with pure pulverized sulphate of lime, exposing a small bead of this mixture supported by a loop of fine platinum wire to the flame of a gas blowpipe and examining the flame with a spectroscope. The characteristic double blue line of rubidium is then seen very distinctly for a few moments, but soon disappears. No trace of cæsium could be discovered, either by the mode of experimenting just described or by examining the platinum salt obtained in the course of the analysis, by the partial precipitation of the alkalies with chlorid of platinum.

Heated alone in a closed glass tube cryophyllite slightly changes color, but gives no sublimate, although when heated in the same with bisulphate of potash it gives a strong reaction of fluorine. When in fine powder, it is completely decomposed after some time even by the dilute mineral acids, the silica separating as a fine powder. From this description it is evident that in its mineralogical characters cryophyllite closely resembles other members of the mica family, especially the lepidolites, differing from these chiefly in the ease with which it is decomposed by acids and in a somewhat greater fusibility.

Method of Analysis.—In analyzing the mineral the fine powder was decomposed in a closed glass flask in the same way as described in my paper on Danalite, using dilute hydrochloric or sulphuric acids as the case required. Each complete analysis was made with three portions of the same powder. From the first

portion, decomposed by hydrochloric acid, the silica, manganese, iron and aluminum were determined, the last two being precipitated as basic acetates and weighed together as oxyds, and the manganese subsequently precipitated from the filtrate by bromine. From the second portion, decomposed by dilute sulphuric acid, with perfect exclusion of air, the amounts of protoxyd and sesquioxyd of iron were determined by means of permanganate of potash, when by subtracting the total quantity of iron, calculated as sesquioxyd, from the sum of the alumina and sesquioxyd of iron already known, the amount of alumina was ascertained. From the third portion of the powder, decomposed by hydrochloric acid, the magnesia and the alkalies were determined. The alkalies were weighed as sulphates, and from the amount of sulphuric acid subsequently determined, the relative quantities of potash and lithia were calculated. From the fourth portion of the powder the quantity of fluorid of silicon was determined. In the first analyses of the mineral the fluorine was precipitated as fluorid of calcium according to the well known method of Berzelius as modified by Rose; but the process was found to be very tedious and the results not accordant. Subsequently the following method was devised, which may be found to be useful in other cases.

Determination of Fluorid of Silicon.—A weighed amount of finely pulverized mineral is first decomposed in a tared platinum dish with dilute sulphuric acid, and the greater part of the water having been removed on a steam bath and the excess of sulphuric acid having been driven off by gradual heating on a sand bath, the whole mass is ignited during at least an hour, the dish meanwhile being covered with a piece of platinum foil forming part of the tare. The dish with its contents having been weighed, the dried mass is next treated with hydrochloric acid and the residual silica determined in the usual way, and in the filtrate from the silica the sulphuric acid is determined and weighed as sulphate of baryta. We thus obtain four weights: A, the weight of the mineral employed in the analysis; B, the weight of the ignited residue; C, the weight of the residual silica; and D, the weight of the residual sulphuric acid. It is now evident that $A+D-B$ equals the weight of the fluorid of silicon, and that $B-C-D$ equals the weight of the sum of all the bases present. The iron is of course present in the residue as sesquioxyd, but in order to ensure its complete oxydation, it is important to add a few drops of nitric acid to the decomposed mineral, before expelling the excess of sulphuric acid. The sum of the weights of all the bases, which we find incidentally as one of the results of this method, not only furnishes an important control of the rest of our analysis, but also enables us to test the accuracy of our method. In the analysis given below it appears that the

sum of the bases each separately determined as the mean of two analyses equals 45·03 per cent, while the sum of the bases weighed together in the method just described equals 45·18 per cent, as the mean of three determinations. A closer agreement than this could not possibly be expected. The process is comparatively short and presents no unusual difficulties. The chief liability to error is in the determination of the sulphuric acid, and it is necessary in washing the sulphate of baryta to take great care to remove the impurities, which this precipitate is apt to carry down; but the methods recommended by Rose and Fresenius were found to be generally sufficient for the purpose. Nevertheless, when the amount of fluorine is less than one per cent, the old process is to be preferred.

Results of Analysis.—Two very distinct varieties of cryophyllite were analyzed,—the one finely foliated and consisting of an aggregate of small crystals and the other in large distinct crystals imbedded in massive feldspar; but no other differences of character were observed, and they were found to have the same percentage composition. The purest material was selected for analysis and such as had evidently never undergone the slightest change. There is probably in all the analyses a small loss of silica, but the error, if any, is in that direction. The results are given in the following table. In columns 1 and 2, we have the complete analyses made as first described of the large crystals, while in columns 3, 4 and 5, we have the partial analysis made of the more finely foliated variety by the process last described in connection with the determination of fluorid of silicon.

Analysis of Cryophyllite from Rockport.

	1.	2.	3.	4.	5.	Mean.	Oxygen.
Silica,	51·53	51·54	51·65	51·37	51·36	51·49	27·46
Fluorid of silicon,			3·29	3·34	3·62	3·42	1·06=28·52
Alumina,	16·76	16·77				16·77	7·82
Sesquioxyd of manganese,	0·33	0·35				0·34	0·10
Sesquioxyd of iron,	2·00	1·94				1·97	0·59= 8·51
Protoxyd of iron,	8·00	7·96				7·98	1·76
Magnesia,	0·76		45·06	45·29	45·02	0·76	0·30
Potassa,	13·14	13·16				13·15	2·23
Lithia,	4·05	4·06				4·06	2·16= 6·45
Soda,	*trace.*					*trace.*	
Rubidia,	"					"	14·96
						99·94	

Oxygen ratio, 14·96 : 28·52
14·26 : 28·52=1 : 2.

General formula, RO, SiO_2. Probable rational formula, $(\frac{1}{3}\dot{R}^3 \,.\, \frac{1}{3}\bar{\bar{R}}), 3\ddot{Si})$.

The fluorine in the mineral is so firmly incorporated that, as stated above, it is not driven out even by a red heat, and there can be no doubt that it replaces a portion of the oxygen of the silica in the proportion of one equivalent of fluorine to every twenty-eight of oxygen. The ratio of the oxygen of the prot-

oxyds to that of the sesquioxyds is as 13 to 17, but if we estimate all the iron as protoxyd, assuming with many mineralogists that a sesquioxyd base may under certain conditions replace a protoxyd base, we shall then have very nearly a ratio of equality and may then write our general symbol $(\frac{1}{2}\dot{R}^3 . \frac{1}{2}\ddot{\ddot{R}}), 3\ddot{S}i$.

As has already been stated, the physical characters of the new mineral do not differ essentially from those of other well known micas, and even its greater fusibility is shared with some varieties of lepidolite, resulting probably from the very large amount of alkali which the silicate contains. The ground on which this mica must be regarded as a new species is the definite oxygen ratio of 1 to 2, which has never before been observed among the micas. The five analyses given above of two distinct varieties, from different localities, differing markedly in appearance, leave no doubt in regard to the definiteness of this ratio, and no more specific character for a new species than this could be desired. When now we consider the very great want of definiteness in the micas as a class, their composition varying between $2RO, SiO_2$ in several varieties, and RO, SiO_2 in cryophyllite, it would appear that the new mica has a distinct typical character, forming as it were one boundary of this family of minerals. Moreover, it is at least a probable theory that the two formulæ just given represent the only two distinct types of micas, and that the variation of composition may result from an admixture of these two isomorphous species. The masterly investigations of De Senarmont on the optical relations of the micas tend to show that such an admixture exists, and at least prove that even a very large difference in the angle of the optical axes does not afford a safe ground for making a distinction in species. He supposed that this difference arises from a mixture of two micas crystallographically isomorphous but optically distinct, the one, and the more common class, having the optical axes in the plane of the longer diagonal, while in the other they fall in the plane of the shorter diagonal, as is the case with cryophyllite. Moreover, he was enabled, by crystallizing together certain isomorphous salts, to produce artificially the same result, which we have naturally in the micas. If then the variation of optical characters results from an isomorphous mixture of *optically* distinct species, it is at least probable that the variation of composition, so far as the oxygen ratio is concerned, may be caused by a similar mixture of *chemically* distinct species, and this view may serve to bring into some sort of order the almost hopeless confusion which the analyses of micas have hitherto presented. The magnesian micas phlogopite and biotite are sufficiently distinguished by the character of their bases, and conform very closely to the general formula $2RO, SiO_2$; but there does not seem to be any good ground for distinguishing between

the two. The optical distinction, as we have seen, is not specific, and if sesquioxyds may replace protoxyds, any apparent difference in the relative proportions of these oxyds is equally of no value as a ground of separation. Even this last difference, however, is not constant, and biotite must be regarded as a phlogopite in which a certain amount of magnesia has been replaced by protoxyd or sesquioxyd of iron. Passing next to lepidomelane, we have a pure iron mica in which all the magnesia has been in like manner replaced. Lastly, the presence or absence of a small and very variable amount of lithia does not seem to make any good ground of distinction between lepidolite and muscovite, and the only essential difference between these species is the much greater fusibility of the former, arising probably from the large amount of alkali and fluorine entering into its composition, a quality which we have endeavored to express by the name cryophyllite, following the analogy of the name cryolite. In lepidolite the oxygen ratio varies very widely between the extreme limits already named, the variation resulting, according to our theory, from a mixture of two species, the first having the type ratio 1 : 1, which we may still call lepidolite, and the second having the ratio 1 : 2, which has been described in this paper and called cryophyllite. A similar admixture of an isomorphous species having the type ratio 1 : 2 may explain the equally wide variations in the oxygen ratio of the muscovite, although the infusible mica corresponding to cryophyllite has not yet been observed. It is manifest that the theory here advanced would be very greatly substantiated if it could be shown that cryophyllite is actually associated with a distinct but isomorphous mica having the type ratio 1 : 1, and that it does actually influence the composition of its associate in the way we have indicated. Such is the case, as we believe, at the Rockport locality.

Lepidomelane.—The mica which is associated with cryophyllite at Rockport (or as we should rather say, with which cryophyllite is associated, for cryophyllite is the subordinate species) is an iron mica of the species lepidomelane. This is the common mica of the great granite ledges which form the extremity of Cape Ann. In the granite itself, however, it occurs only in small flakes forming a very small proportion of the whole mass; but in the numerous veins which intersect the rock, lepidomelane is found in crystals of considerable size and sometimes in plates several inches in diameter. The vein, from which most of the best specimens have been taken, is an offshoot of one of the great trap dikes which cross the Cape from north to south nearly parallel to each other, and consists chiefly of massive quartz and feldspar almost completely segregated, the quartz lining the lower wall, while the feldspar lines the hanging wall

of the vein. The best crystals, both of lepidomelane and of cryophyllite, are found in the massive feldspar, sometimes in direct contact and interpenetrating each other, while at other times they are comparatively isolated. The crystals of the two minerals resemble each other so closely in their external aspect that it requires some experience to distinguish them, without applying the distinctive test soon to be mentioned, and even an experienced mineralogist might readily mistake an aggregate of the two for a homogeneous mass. Like cryophyllite the lepidomelane crystallizes in hexagonal prisms with an angle of 120° between the prismatic planes, as was measured on several specimens with an application goniometer. Moreover the crystals have the same general habitus as those of the associated mica. They are frequently seen elongated in the direction of the brachydiagonal and twinned together on the plane *iĭ*, and, in a word, the description of the crystals of cryophyllite already given applies equally well to those of lepidomelane; but unfortunately on account of the great opacity of lepidomelane I have not yet succeeded in determining its optical relations. There can be no doubt, therefore, that the two micas are perfectly isomorphous. But while the outward resemblance of these micas is so striking, the mineralogical characters of the two species are wholly distinct, as will be seen from the following description.

Mineralogical characters of Rockport Lepidomelane.—The cleavage is basal and perfect, but it is not so eminent as in most micas, and the foliæ are not at all or only slightly elastic. The color is black, and that of the streak dark green, differing wholly from the color of the streak of cryophyllite, which is light gray with only a faint tinge of green. The laminæ are opaque unless exceedingly thin. The luster is very brilliant, inclining to resinous on the cleavage face. The sp. gr. was found to be 3·169, and the hardness about that of calcite, or 3. Before the blowpipe it fuses to a black enamel bead, which is highly magnetic, and this affords another ready means of distinguishing it from cryophyllite. The fusibility is about that of iron-garnet, or between 3 and 4 of von Kobell's scale. With borax it forms a bottle-green glass. The powder when heated in a closed glass tube gives off water, and its green color changes to a pinchbeck-brown not unlike that of magnetic pyrites. Heated with bisulphate of potash it gives a slight reaction for fluorine. The powder is easily decomposed by the dilute mineral acids, the silica separating in fine scales. These characters agree very closely with those of the original lepidomelane from Wermland as described by Soltmann,* only the more perfect crystals from Rockport enable us to determine the crystalline form with more cer-

* Pogg. Annalen, l, 664, also Dana's System, 4th edition, vol. ii, page 297.

tainty than was possible with the minute scales from which the species was first established.

Analysis of Rockport Lepidomelane.—My analyses of this mica are given in the following table. In the analyses 2, 3, and 4, the same methods were followed which have already been described in connection with cryophyllite. In analysis 5, I employed, with some slight modification, the method first proposed by H. Saint Claire Deville,* and the close agreement of the figures obtained by such very different methods serves to confirm the general accuracy of the result. The determination of the water was the chief difficulty met with in the analyses. The water enters so intimately into the composition of the mineral that it is not expelled below a low red heat, and then only quite slowly. Moreover at this temperature the mineral is rapidly oxydized. But by igniting the mineral in a current of carbonic acid gas the oxydation was prevented and constant results were obtained. With this precaution portions of the same powder were ignited, first without and then with oxyd of lead with the following results:

	1.	2.	3.	Mean.
Loss on ignition without PbO,	1·54	1·52	1·52	1·53
" " with "	1·55	1·40		1·48

The difference is within the limit of probable error, and the results prove that the fluorine is not expelled at a low red heat. Moreover the mineral after ignition gave as strong a reaction for fluorine as before, and when heated to the highest temperature which could be obtained with a gas blast lamp, underwent no farther loss of weight. This is in accordance with what we found to be true of cryophyllite; but not in accordance with the comportment of hydrous minerals into which fluorine enters as an essential constituent. Compare analyses of Cookeite, this Journal, [2], xli, 246. These facts, taken in connection with the circumstance that fluorine was not found by Soltmann in the lepidomelane of Wermland, lead to the inference that the fluorine in the Rockport mineral is an accidental constituent, derived from the admixture of material foreign to the species itself. The amount of fluorid of silicon in analysis 2 was determined by the method of Berzelius; but the limit of error in this process is so wide that the result can only be regarded as approximate. The analyses which follow were all made on material dried at 100°, and selected to represent the different varieties of the mineral found at Rockport. Analyses 2 and 3 were made from portions of a mass of comparatively compact material. No. 4 from a perfect crystal imbedded in the massive feldspar of the vein already referred to, and the silica determination. No. 1 from scales picked out from the granite of Boylston Hall in Cambridge, which is built of stone from the Rockport quarries.

* Annales de Chimie et de Physique, [3], xxxviii, 5.

Analysis of Rockport Lepidomelane.

	1.	2.	3.	4.	5.	6.	7.	8.	Mean.	Oxygen.
Silica,	39·50	39·49	—	39·79	39·48	—	—	—	39·55	21·09
Fluorid of silicon,		0·62	—	—	—	—	—	—	0·62	0·19=21·28
Alumina,		16·72	16.41	16·90	16·87	—	—	—	16·73	7·81
Sesquiox. of manganese,		—	0·63	0·58	0·59	—	—	—	0·60	0·18
Sesquiox. of iron,		—	—	—	—	12·21	12·01	11·98	12·07	3·62
Protox. of iron,		—	—	—	—	17·57	17·47	17·41	17·48	3·88
Magnesia,		—	—	0·64	0·59	—	—	—	0·62	0·25
Potassa,		—	—	10·68	10·63	—	—	—	10·66	1·81
Lithia,		—	—	0·60	0·57	—	—	—	0·59	0·32
Soda,		—	—	—	—	—	—	—	*trace.*	—
Rubidia,		—	—	—	—	—	—	—	"	—
Water,		—	—	1·55	1·40	1·52	1·52	1·54	1·50	1·33=19·20
									100·42	

Oxygen ratio, 19·20 : 21·31.

After an examination of the results of the above analyses no one can doubt that the true oxygen ratio of the mineral is 1 : 1, and that the general formula is $2RO, SiO_2$ or $2(\frac{1}{2}\dot{R}^3 . \frac{1}{2}\ddot{R})3\dddot{Si}$. This is not only the nearest probable formula, but moreover it harmonizes with the well established formulæ of allied species and with the results of Soltmann's analysis of lepidomelane, a mineral which our Rockport mica resembles most closely in all its characters. Nevertheless the discrepancy between the actual and the probable ratio is very great, and cannot possibly be referred to impure material or imperfect processes. As has been already stated, the material used in the fourth analysis was a portion of a perfect crystal completely isolated in a mass of feldspar, and the results of this analysis agree almost precisely with those obtained in No. 5 by an entirely different process and with wholly different material. Here then are the same unsatisfactory results, which have been obtained again and again in the analyses of the micas, and have made it so difficult to reduce to order this important family of minerals. Fortunately we find at the Rockport locality what I believe to be the clue to the whole mystery. The common mica of the granite is there associated with a second mica containing twice as much silica, but still perfectly isomorphous with it in crystalline form. Now if two isomorphous salts crystallize together from the same solution, we obtain crystals which are mixtures of the two in definite proportions, the proportions depending chiefly on the relative quantity of each which may be present; but also at times on other conditions less accurately determined.* When the sedimentary rocks were undergoing the metamorphism which converted them into the granite ledges of Rockport, or when by any other means this granite was formed, the two isomorphous micas, described in this paper, did actually crystallize together, for so we find them; and it is reasonable to suppose that the same results followed in the one case as in the other, and that

* See Rammelsberg's important paper on this subject, Pogg. Ann., xci, 321.

the mica of the Rockport granite is an isomorphous mixture of these two distinct species. This conclusion, moreover, is favored by the fact that lepidomelane—the species to which this mica undoubtedly belongs—contains in other localities neither lithia nor fluorine; while on the other hand these same ingredients are strikingly characteristic of the lepidolite micas, to which cryophyllite is allied. Assuming then that the lithia and fluorine in the analyses belong to the cryophyllite and not to the lepidomelane, we have endeavored in the following table to eliminate this disturbing element from our results. Thus, in column 1 we have repeated the mean result of our analyses. In column 2 we have the amounts of the several ingredients of cryophyllite corresponding to 0·59 per cent of lithia, deduced from the analyses of this mineral given above. Subtracting these quantities from those in the first column we have the numbers in the third column. In column 4 we have reduced the same to a percentage composition, and these numbers, according to our theory, represent the true composition of the Rockport lepidomelane. In column 5 we have placed for comparison the analysis of lepidomelane by Soltmann.

Reduction of analyses of Lepidomelane.

	1.	2.	3.	4.	Oxygen.	5.	Oxygen.
Silica,	39·55	7·48	32·07	**37·39**	....=19·94	**37·40**	=19·94
Fluorid of silica,	0·62	0·50	....	....	....		
Alumina,	16·73	2·44	14·29	**16·66**	7·78	**11·60**	5·42
Sesquiox. of manganese,	0·60	0·05	0·55	**0·64**	0·19		
Sesquiox. of iron,	12·07	0·29	11·78	**13·74**	4·12	**27·66**	8·29
Protoxyd of iron,	17·48	1·16	16·32	**19·03**	4·28	**12·43**	2·76
Magnesia,	0·62	0·11	0·51	**0·59**	0·24	**0·26**	0·10
Potassa,	10·66	1·91	8·75	**10·20**	1·73	**9·20**	1·61
Lithia,	0·59	0·59	....	....	....		
Water,	1·50	....	1·50	**1·75**	1·56=19·85	**0·60**	0·53=18·71
				100·00		**99·15**	

Oxygen ratio, 19·85 : 19·94 = 1 : 1.

General formula 2RO, SiO_2. Probable rational formula, $2(\frac{1}{3}\dot{R}^3, \frac{1}{3}\ddot{\bar{R}})3\ddot{Si}$.

The result of our calculation, as will be seen, is most satisfactory; for not only is the oxygen ratio thus obtained exact, but also the numbers agree very closely with those of Soltmann, the only apparent discrepancies disappearing when the sum of the alumina and the oxyds of iron and manganese are compared together in the two analyses, and the difference in the distribution of the iron between the two oxyds is unimportant if we assume as before that the oxyds may replace each other. We have estimated in both analyses the amount of water among the bases for the following reasons, which seemed to us conclusive: first, because the loss of water is attended by a very marked change in the color of the mineral—from green to brown—

proving that the water must be chemically, and not merely hygroscopically, combined; secondly, because while water of crystallization would be present in a definite number of equivalents —one or more—the quantity of water in this mineral obeys no such law, and only amounts to a small fraction of a single equivalent; lastly, because the water is only driven out at a high temperature, indicating that it is in a state of intimate combination. There does not appear to be any simple relation between the amounts of the protoxyd and sesquioxyd of bases in the Rockport lepidomelane; but the general formula of the mineral may readily be reduced to that of the magnesian micas by assuming that a portion of the protoxyd of iron has been replaced by the sesquioxyd.

The facts advanced in this paper seem to show quite conclusively that the variation in composition of the Rockport lepidomelane from the normal type is caused by the admixture of a second isomorphous mica with a higher oxygen ratio, which we have called cryophyllite, and this being the case we may expect to find that similar variations in the composition of other micas are due to a similar cause, and it will therefore be interesting to search for the disturbing element at the various localities. Such an examination will be likely to reveal either the presence of cryophyllite itself or else of some new species analogous to it; and if the Rockport locality is any guide, such minerals are more likely to be found in feldspathic veins or nodules of the granite rather than uniformly diffused through the rock itself. It is a fact worthy of notice, and which is quite evident from the above analyses, that the proportions in which cryophyllite is mixed with lepidomelane are quite constant throughout the Rockport locality; and this again is wholly in accordance with the well known facts which have been developed by Rammelsberg* and others in regard to the crystallization of isomorphous salts when mixed together in the same solution. It appears from these investigations that isomorphous salts do not necessarily crystallize together in every proportion, but that, in most cases at least, any two given salts have, so to speak, a definite capacity for each other, and that when the point of saturation is passed, pure crystals of the salt in excess may be deposited in direct contact with those which are mixtures of the two. Such experiments furnish an exact counterpart of the conditions which we actually realize in the Rookport granite.

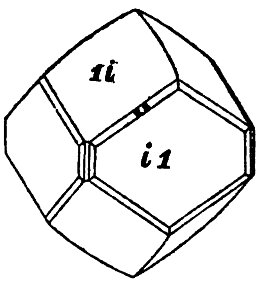
Albite.—The general nature of the vein in which the best crystals, both of cryophyllite and lepidomelane, have been found, has already been described in the earlier part of this paper. This vein consists chiefly of quartz and feldspar of the ortho-

* Pogg. Ann., vol. xci, p. 321.

clase variety. Very fine green colored crystals of the last have been obtained here, and good crystals of the usual color are abundant. Associated with the orthoclase I have frequently noticed a compact variety of albite distinguished by a peculiar luster and very marked striation on the plane of easy cleavage. It resembles somewhat, in outward aspect, oligoclase, but the mineral had the characteristic cleavages of a clinoclase feldspar, and the angle *O* on *i*ĭ measured with an application goniometer 93°. Moreover it contains, if any, only the merest trace of lime. The albite is actually imbedded in the orthoclase, and the intimate association of these two heteromorphous species is worthy of notice.

Malacone.—The same vein contains also a peculiar variety of zircon, which is probably identical with the malacone of Scheerer, only somewhat more altered. The crystals have the general form represented in the figure, and resemble the crystals of zircon from Expailly in France. On account of the great predominance of the planes 1*i* and *i*1, they resemble the rhombic dodecahedron of the regular system, and can only be distinguished from this form by the distribution of the modifying planes; since on account of the strong curvature of the faces the limits of necessary uncertainty in the measurement of the angles cover the whole difference between this form and the corresponding form of zircon. In the ordinary method of representing the crystals of zircon the relation of the forms just referred to does not appear; but if we refer the planes of the zircon crystals to axes corresponding in position to those of the allied form of the regular system, the really close affinity of the two becomes evident. Thus the ratio of the axes, which in the regular system is unity, is in zircon $a : b = 0{\cdot}906 : 1$, and the angle 1*i* on *i*1, which in the dodecahedron equals 120°, is in the zircon crystal equal to 123° 19′. In the figure here given the crystal has been drawn and the planes lettered with reference to the axes of the dodecahedron, and this must be borne in mind when comparing it with other figures of zircon. The most striking peculiarity of the crystals is the strong curvature of the terminal faces, which has been indicated in the figure, and which, as already intimated, renders accurate measurements impossible. Nevertheless, within the limits of necessary uncertainty the angles measured the same as those of zircon. The small planes not lettered on the crystal for want of space are *ii* and *i*3.

2.



The color both of the crystal and the powder is brownish-red,

and this color is not altered by ignition. Luster more or less adamantine on different specimens, evidently varying with the degree of alteration, and becoming more brilliant after ignition. Fracture after ignition conchoidal and very brilliant, but varying on the natural crystals, like the luster, with the degree of alteration. There is no distinct cleavage. Hardness before ignition from 5 to 5·5; after ignition from 7 to 7·5. Specific gravity before ignition from 3·985 to 4·040, the extreme limits observed; after ignition 4·095. Before the blowpipe the mineral is infusible. In a closed tube it gives off water, which has at first an alkaline reaction, but becomes acid when the mineral is heated more intensely. With bisulphate of potash gives slight reaction for fluorine. The powder dissolves with some difficulty in melted borax, giving only the reaction for iron. In phosphorus salt it dissolves only with great difficulty and incompletely, giving in the reducing flame, even when treated with tin on charcoal, a colorless glass. The mineral is partially decomposed by hydrochloric acid; more perfectly by strong sulphuric acid, and completely by fusion with carbonate of soda. An imperfect analysis gave the following results:

Silica, - - - - - - - - -	27·90
Zirconia, - - - - - - - - -	66·93
Sesquioxyd of iron with trace of manganese, -	2·57
Water, - - - - - - - - -	2·19
	99·59

These numbers must give very nearly the composition of the material analyzed; but the composition must vary with the degree of alteration, and probably no two specimens would give precisely the same result. The material used was the best I could command, but not so good as might be desired, and I am happy to learn that a more trustworthy analysis will soon be published. On comparing these numbers with Scheerer's analyses of malacone, it appears that the amount of silica is somewhat greater in the original specimens, but the difference is evidently the result of further alteration. The zirconia was examined for other earths and metallic oxyds, but without positive results. No distinct indications of titanium could be obtained with the blowpipe, although it is possible that in the presence of so large an amount of zirconia a small amount might have escaped notice. The zirconia separated from the mineral was converted into chlorid, and the solution when evaporated crystallized to the last drop, forming a large mass of white silky needles. A solution of this chlorid, still acid to litmus paper, turned turmeric paper orange-yellow. In a solution of the same chlorid, oxalic acid produced a voluminous precipitate, which, when the solu-

tion was cold, readily dissolved in an excess of the reagent, and the more readily the larger the quantity of free hydrochloric acid present. If the solution was heated to boiling during the precipitation, the precipitate was not easily redissolved; but by digesting it for several hours with a very large excess of oxalic acid complete solution was finally effected. In a similar solution of the chlorid, a strong solution of sulphate of potash produced a precipitate, which in the presence of free hydrochloric acid readily dissolved in an excess of the reagent if the solution was kept cold. But if the solution was heated during the precipitation, the precipitate did not thus redissolve; but it immediately disappeared on adding a small amount of dilute sulphuric acid. From a solution of the chlorid of zirconium, ammonia throws down a gelatinous precipitate, but this precipitation was entirely prevented by the addition of tartaric acid. The hydrate thus obtained, when heated before the blowpipe, became intensely luminous and changed into a hard granular powder insoluble in all dilute acids. After digesting it, however, for several hours in strong sulphuric acid, it was converted into a sulphate, which dissolved completely on diluting the acid with water. These reactions appear to indicate that the zirconia was quite, if not entirely, free from an admixture of other earths, and the manner in which its reactions are modified by the temperature is the probable explanation of the confusion on the subject which is found in many text-books. The two modifications of zirconia, distinguished by Berzelius, seem to be repeated in many of its compounds, and malacone stands in the same relation to ordinary zircon that the soluble oxalate and sulphate do to the insoluble varieties. The malacone at Rockport is unquestionably in process of alteration, but whether the original mineral was the ordinary zircon or what we may call the normal malacone, I have not yet been able to determine.

CHILDRENITE FROM HEBRON IN MAINE.

[FROM THE AMERICAN JOURNAL OF SCIENCE AND ARTS, VOL. XXXVI, SEPT., 1863.]

ON CHILDRENITE FROM HEBRON IN MAINE.

BY GEO. J. BRUSH.

IN an article on the occurrence of *amblygonite* at Hebron, published in this Journal, vol. xxxiv, p. 243, 1862, I mentioned that it was sometimes associated with a peculiar compact variety of apatite, containing minute prismatic crystals of a hair-brown mineral. The small amount of this hair-brown mineral, at that time in my possession, prevented me from determining fully its specific characters; but subsequent explorations of the Hebron locality, made by Mr. Oscar D. Allen, have furnished a sufficient quantity of the substance for examination, to lead to the conclusion that the mineral is probably a variety of *childrenite.*

It occurs in minute prismatic crystals, rarely over three lines in length and half a line in breadth and height: a full description of the crystalline form together with a comparison with the Tavistock childrenite is given beyond by Professor Cooke. Its other characters are as follows. Hardness=5. Specific gravity =3·03 (taken on less than half a gramme of fragments of crystals). Color dark hair-brown. Translucent. Lustre vitreous and brilliant. Streak white. Fracture uneven. Many of the crystals are partially decomposed, and converted into a lustreless earthy material. When heated in the closed tube, the unaltered mineral gives off neutral water, and the ignited residue is magnetic. Before the blowpipe in the forceps it swells up into ramifications and fuses on the edges, giving the flame a pale-green color, indicative of phosphoric acid. Fusibility=4, on v. Kobell's scale. Heated on charcoal becomes magnetic; with soda in the platinum loop gives a strong reaction for manganese; with borax and salt of phosphorus gives reactions for both manganese and iron. Decomposed by chlorhydric acid leaving traces of silica as an insoluble residue. Qualitative analysis proved the mineral to be a hydrous phosphate of iron, alumina and manganese.

This composition, together with the physical and pyrognostic characters, seem to indicate that the mineral is identical with *childrenite*, a view that is further supported by the crystallographic examination made by Professor Cooke. Only a very few specimens of the Hebron childrenite have as yet been found. This rare species has never before been observed in America.

CRYSTALLOGRAPHIC EXAMINATION OF THE HEBRON MINERAL,

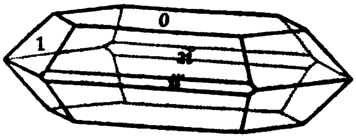
AND COMPARISON OF IT WITH THE CHILDRENITE FROM TAVISTOCK.

By J. P. COOKE, Jr.

The measurements, which I have made of the crystals from Hebron, sent me by Professor Brush, have afforded the following results.

Form trimetric.—Ratio of axes
$a : b : c = 0·977 : 1 : 1·482$.

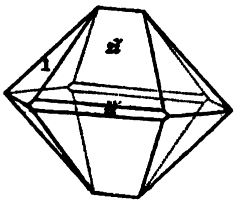
1.



	Observed.	Calculated.
1 on 1 (mac.)	129° 30′*	
1 on 1 (brach.)		101° 36′
1 on 1 (basal)		99° 22′
O on 2ĭ	127° 10′*	
2ĭ on 2ĭ (over *O*)	74° 20′	74° 22′

For comparison with the above, I have made the following measurements and figure of the childrenite of Tavistock in Devonshire, England.

2.



Ratio of axes—$a : b : c = 0·969 : 1 : 1·493$.

	Observed.	Calculated.
1 on 1 (mac.)	130° 10′*	
1 on 1 (brach.)	101° 43′*	
1 on 1 (basal)	98° 44′	98° 40′
2ĭ on 2ĭ (over *O*)		75° 24′

The values asterisked are in both cases those used in calculating the angles given in the second column. The faces 1 and 2ĭ, both on the crystals from Hebron and the specimens of childrenite from Tavistock, are so strongly striated parallel to the basal edges that only a few of the angles can in either case be accurately measured. Three of the Hebron crystals and two crystals of the Tavistock childrenite were examined, and the same angles on the different specimens of the same kind were found to agree very closely with the values given above in the column headed 'observed,' the extreme difference not exceeding four or five minutes, which is about the limit of the probable error of the measurements. The angles not given in this column were incapable of exact measurement on the specimen examined, on account of the striation just noticed. Although there is a difference of over half a degree in one of the fundamental angles, yet the general crystallographic characters of the two

sets of crystals (the striation and lustre of the different faces) are so nearly the same, that there can be no doubt that the Hebron crystals are a variety of childrenite, differing perhaps from the English childrenite in some not fundamental point of chemical composition.

It will be noticed from the figures (in which the relative proportions of the planes have been preserved as nearly as was possible by the eye) that while on the Tavistock crystals the basal plane is wanting, it is very prominent on the specimens from Hebron, and gives to the crystals from this locality their marked prismatic character. This difference, although from our present mineralogical stand-point unimportant, nevertheless wholly alters the general appearance of the crystal, so that while the Hebron crystals are prismatic, and elongated in the direction of the brachydiagonal, the Tavistock crystals are pyramidal.[1] That differences like this, and even slight differences of angle may be occasioned by the nature of the material in which the mineral crystallized is generally admitted. When, therefore, we consider the peculiar character of the gangue in which the Hebron crystals were found, so different from that at Tavistock, we can hardly be surprised at differences of crystalline form as great as those described above. As already stated, the angles of the Hebron crystals above given are accurate only within four or five minutes, and it is to be hoped that, on further working the locality, more perfect crystals will be found, which will enable us to correct, if necessary, the above measurements.

[1] At least this is true of all the specimens which have fallen under my observation, but in the original figure of the Tavistock crystals by Brooke, (Brande's *Quarterly Journal*, xvi, 274, and Dana's *Manual of Mineralogy*, ii, 424,) not only the basal plane O but also a second set of octahedral planes $\frac{1}{2}$ are represented. This figure in general appearance resembles quite closely the Hebron crystals and is very different from the pyramidal form we have given above. The difference is probably to be explained by the varying characters of the matrix in which the crystals occur at that locality, and it shows that, under certain conditions, the mineral has a tendency to the prismatic form which is only more fully developed in the specimens from Hebron.

[From the American Journal of Science and Arts, Vol. XLVII, May, 1869.]

ATOMIC RATIO.

BY JOSIAH P. COOKE, JR.

The so-called *oxygen ratio*, used by mineralogists, when interpreted by the new chemical philosophy, is simply the ratio between the total quantivalences of the several classes of radicals, which enter into the composition of a mineral. Indeed its whole value as a specific character in mineralogy depends upon the fact that it expresses this fundamental relation between the different atoms, which are associated in the molecules of the compound, and we propose therefore to call it the *Atomic Ratio.*

The possible hydrates of silicon may be represented by the general formula

$$n(H_4{\equiv}O_4{\equiv}Si)-mH_2O=H_{4n-2m}O_{4n-2m}Si_nO_m,$$

and every silicate may be regarded as derived from the corresponding hydrate by replacing the hydrogen atoms to a greater or less extent. Thus the composition of garnet is shown best by*

$$\overset{ii}{R}_3,[\overset{vi}{R}_2]\,{}^{xii}O_{12}{}^{xii}\overset{iv}{Si}_3$$

in which $\overset{ii}{R}$ may be either Ca, Mg, Fe, Mn or Cr, and $[\overset{vi}{R}_2]$ either $[Al_2]$, $[Fe_2]$ or $[Cr_2]$. Garnets have been analyzed, in which these several radicals are mixed together in every conceivable way consistent with this general formula, to which they all conform. This formula expresses all that is constant so far as the composition of the mineral is concerned, and the constant element is merely a definite ratio between the quantivalences, or atomicities, of the several classes of radicals taken collectively. In the last analysis this ratio is the one specific character, which distinguishes many mineral species, and hence its importance in the science of mineralogy.

When the general formula of a mineral is given we can easily calculate the atomic ratio. We have simply to *multiply the number of atoms of each radical by its quantivalence and find the simplest ratio between these products,* and this rule holds in whatever form the symbol may be written. Thus the atomic ratio of garnet is 6 : 6 : 12 or 1 : 1 : 2. So in like manner the ratio for orthoclase is 2 : 6 : 24 or 1 : 3 : 12. On the

* The system of notation here used is explained at length in the author's work on Chemical Philosophy recently published. The main feature of the system consists in writing the symbols in a linear form and separating by commas the several radicals, which, although united to the same central or determinant atom, are otherwise independent of each other, Figures below the symbols indicate independent atoms, except when the symbol is enclosed in brackets. These show that the atoms are united among themselves to form a compound radical and that in consequence two or more of their affinities are closed. Dashes are used to point out the directions in which the several affinities of the principal radicals are exerted, but when the number of dashes required becomes inconveniently large they are indicated by Roman numerals. The Roman numerals above the symbols indicate as usual the quantivalence of the radicals.

other hand from the ratio we can as easily construct the symbol. For example the ratio in the case of anorthite is 1 : 3 : 4. By doubling this, (2 : 6 : 8) we make the first term divisible by 2, the second by 6, and the third by 4 the quantivalences of the several radicals associated in the mineral. Thus we have the skeleton as it were of the mineral $\overset{ii}{R}$, $[\overset{vi}{R_2}]$, $\overset{iv}{Si_2}$ and we now easily add the number of oxygen atoms required to "close" the molecular group, which gives us for the full symbol $\overset{ii}{R}$, $[\overset{vi}{R_2}]^{viii}O_8{}^{viii}Si_2$. In like manner from the ratio 1:3:6 we first deduce the number of atoms of the three radicals, namely $\overset{ii}{R}$, $[\overset{vi}{R_2}]$, Si_3 and then we add, besides the eight atoms of oxygen required to unite the basic radicals to the atoms of silicon, also two more to "close" the molecule.

The atomic ratio is easily deduced from the results of analysis by simply extending the usual method for finding the symbol of a body, whose molecular weight is unknown. We assume that the molecular weight is 100, and having divided in the usual way the per cent of each radical by its atomic weight we *multiply the several quotients by the quantivalence of the respective radicals.* Lastly we add together these products for each class of replacing radicals, and compare the several sums thus obtained. For example Moberg's analysis of the Bohemian pyrope gave the following results.

Si	19·30	or	SiO_2	41·35
$[Al_2]$	11·92		Al_2O_3	22·35
Fe	7·73		FeO	9·94
Mn	2·01		MnO	2·59
Mg	9·00		MgO	15·00
Ca	3·77		CaO	5·29
Cr	3·19		CrO	4·17
O	43·77			
	100·69			100·69

Dividing now each per cent by the atomic weight of the radical and multiplying by its quantivalence we obtain the following numbers:

Si	$(19{\cdot}30 \div 28) \times 4 = 2{\cdot}76$		**2·76**
$[Al_2]$	$(11{\cdot}92 \div 54.8) \times 6 = 1{\cdot}31$		**1·31**
Fe	$(7{\cdot}73 \div 56 \times 2 = 0{\cdot}27$		
Mn	$(2{\cdot}01 \div 55 \times 2 = 0{\cdot}07$		
Mg	$(9{\cdot}00 \div 24 \times 2 = 0{\cdot}75$		
Ca	$(3{\cdot}77 \div 40 \times 2 = 0{\cdot}19$		
Cr	$(3{\cdot}19 \div 52{\cdot}2) \times 2 = 0{\cdot}12$		**1·40**

whence we deduce the ratio

1·40 : 1·31 : 2·76 or 1 : 1 : 2 nearly.

It is usual in works on mineralogy to present the results of

analysis on the old dualistic plan, as if the mineral were formed by the union of various basic anhydrids with silica. Starting with such data it is not, however, necessary to calculate the per cent of each radical in the assumed anhydrids before applying the above rule, because, obviously, by dividing the per cent of each anhydrid by its molecular weight we shall obtain the same quotients as before. For example, in the analysis of garnet cited above, where the data are given on one side in the usual form, we have

$$\overset{28}{Si} : \overset{60}{SiO_2} = 19{\cdot}30 : 41{\cdot}35 \text{ or } 19{\cdot}30 \div 28 = 41{\cdot}35 \div 60$$

and so for each of the other values.

In the symbols of the silicates as formerly written on the dualistic theory the atoms of oxygen were necessarily apportioned among the different radicals in proportion to their quantivalence, although this fundamental distinction between them was itself overlooked. Thus the general symbol of garnet would be written dualistically thus:

$$3RO, R_2O_3, 3SiO_2$$

and it is evident that the number of oxygen atoms is in each case a measure of the relative quantivalences of the radicals, with which they are associated. Hence the atomic ratio might also be found by comparing together the quantities of oxygen, which the several assumed anhydrids contain, and this is the manner, in which the calculation has generally been made hitherto. Hence also the reason that the atomic ratio has been called the oxygen ratio and was long used in mineralogy before its true meaning was understood. But although the old method gives the same results as the new, it is not in harmony with our modern theories and is practically less simple. Moreover, the principle is far more general than the old method would imply and may be used with all classes of compounds as well as with those, in which the radicals are cemented together by oxygen. Furthermore it is frequently useful to compare the atomic ratios of the complex radicals which may be assumed to exist in different minerals, and interesting relations may frequently be discovered in this way, which the old method would entirely overlook. Thus for example the symbols of the more important feldspars, clays and zeolites may be written in the following form:

Feldspars.

Anorthite,	Triclinic,	$Ca, [Al_2]^{viii}O_8{}^{viii}Si_2$
Labradorite,	"	$[Na_2, Ca], [Al_2]^{viii}O_8{}^{viii}Si_3O_2$
Leucite,	Isometric,	$K_2, [Al_2]^{viii}O_8{}^{viii}Si_4O_4$
Oligoclase,	Triclinic,	$[Ca, Na_2], [Al_2]^{viii}O_8{}^{viii}Si_5O_6$
Albite,	"	$Na_2, [Al_2]^{viii}O_8{}^{viii}Si_6O_8$
Orthoclase,	Monoclinic,	$K_2, [Al_2]^{viii}O_8{}^{viii}Si_6O_8$

Clays.

Kaolinite,	Orthorhombic,	$H_2, [Al_2]^{viii}O_8{}^{viii}Si_2 . H_2O$
Halloysite,	Massive,	$H_2, [Al_2]^{viii}O_8{}^{viii}Si_2 . 2H_2O$
Pyrophyllite,	Orthorhombic,	$H_2, [Al_2]^{viii}O_8{}^{viii}Si_3O_2$
Agalmatolite,	Massive,	$H_2, [Al_2]^{viii}O_8{}^{viii}Si_4O_4$

Zeolites.

Thomsonite,	Orthorhombic,	$[Na_2,Ca], [Al_2]^{viii}O_8{}^{viii}Si_2 . 2\frac{1}{2}H_2O$
Natrolite,	"	$Na_2, [Al_2]^{viii}O_8{}^{viii}Si_3O_2 . 2H_2O$
Scolecite,	Monoclinic,	$Ca, [Al_2]^{viii}O_8{}^{viii}Si_3O_2 . 3H_2O$
Analcime,	Isometric,	$Na_2, [Al_2]^{viii}O_8{}^{viii}Si_4O_4 . 2H_2O$
Chabazite,	Hexagonal,	$Ca, [Al_2]^{viii}O_8{}^{viii}Si_4O_4 . 6H_2O$
Harmatome,	Orthorhombic,	$Ba, [Al_2]^{viii}O_8{}^{viii}Si_5O_6 . 5H_2O$
Heulandite,	Monoclinic,	$Ca, [Al_2]^{viii}O_8{}^{viii}Si_6O_8 . 5H_2O$
Stilbite,	Orthorhombic,	$Ca, [Al_2]^{viii}O_8{}^{viii}Si_6O_8 . 6H_2O$

And it will be seen that the atomic ratio of the basic radicals to the various complex acid radicals is the same for all these minerals, although the ratios of the basic radicals to the silicon alone are quite different. The last, however, vary according to a simple law and indicate a still further relation between the several species. These relations may be discovered by a simple inspection of the symbols, but they will be rendered much more striking by tabulating the atomic ratios deduced as above.

Lastly, the atomic ratios express the results of analysis in the simplest possible terms and in a form, in which they can be most readily compared in various combinations, and such combinations bring out unexpected results. Thus the atomic ratio of zircon $Zr \equiv O_4 \equiv Si\,(4:4)$ is the same as that of garnet, when the sum of all the basic radicals is compared with the silicon, and the two minerals although belonging to different systems have nevertheless very nearly the same crystalline form. Again, zircon is isomorphous with tin-stone and rutile. Now the total quantivalence of all the radicals both basic and acid in each of these minerals (taking the symbols as they are usually written) is a multiple of four and there are reasons for believing that the molecules of the three, last named, are more condensed than the common symbols would indicate. It is therefore possible that all four may have a similar constitution as is shown in the following table, and the important class of minerals of which spinel is the type may be included in the same scheme.

Tin-stone	SnO_2	or	$Sn_3{}^{xii}O_{12}{}^{xii}Sn_3$
Rutile	TiO_2	or	$Ti_3{}^{xii}O_{12}{}^{xii}Ti_3$
Zircon	$Zr \equiv O_4 \equiv Li$	or	$Zr_3{}^{xii}O_{12}{}^{xii}Si_3$
Garnet			$R_3, [R_2]^{xii}O_{12}{}^{xii}Si_3$
Spinel	$R, [R_2]^{viii}O_4$	or	$R_3, [R_2]^{xii}O_{12}{}^{xii}[R_2]_3$

Such facts as these do not of course prove anything. They are however suggestive, and are adduced because they illustrate the use that may be made of this principle of atomic ratios.

[*From the Author.*]

III.

THE VERMICULITES:

THEIR CRYSTALLOGRAPHIC AND CHEMICAL RELATIONS TO THE MICAS;

TOGETHER WITH A DISCUSSION OF THE CAUSE OF THE VARIATION OF THE OPTICAL ANGLE IN THESE MINERALS.

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Read, Dec. 9, 1873.

Introduction. — In the American Journal of Science (VII. 55, 1824), T. H. Webb described a mineral from Millbury, near Worcester, Mass., which has since been a mineralogical curiosity on account of its singular reaction when heated. The mineral consists of "small foliated scales distributed through a steatitic base." "When heated, it exfoliates prodigiously, the scales opening out into long worm-like threads made up of the separate foliæ. Exfoliation commences at 500° to 600° Fahr., and takes place with so much force as often to break the test-tube in which the mineral may be confined. Before the blowpipe it fuses at 3.5 to a grayish-black glass." It was named by Webb, as he says, "from the Latin *vermiculor*, 'I breed worms.'" The hardness of the mineral is 1–2, the specific gravity 2.756, the lustre talcose, and the color grayish, somewhat brownish. It was analyzed by Crossley, who "separated with great care from the base the scaly mineral, which is the true vermiculite," and his results were as follows:—

	1.		*Oxygen Ratio.* True	*Oxygen Ratio.* App.	2.		*Oxygen Ratio.* True	*Oxygen Ratio.* App.
Silica . . .	35.74	19.06	19.06	11	35.74	19.06	19.06	2
Alumina . .	16.42	7.65	7.65	4	16.42	7.65		
Ferric Oxide .					11.13	3.34	10.99	1
Ferrous Oxide	10.02	2.23						
Magnesia . .	27.44	10.98	13.21	7	27.44	10.98	10.98	1
Water . . .	10.30	9.16	9.16	5	10.30	9.16	9.16	1
	99.92				101.03			

The results of analysis in column 1, and the portions of the description of the mineral in quotation-marks, above, have been taken from "Dana's System of Mineralogy," fifth edition, page 493; and the atomic ratio which is there deduced is,

$$\overset{IV}{Si} : \overset{VI}{R} : \overset{II}{R} : \overset{II}{H} = 11 : 4 : 7 : 5.$$

In this analysis, however, Crossley could not have determined the state of the iron, which, in the specimen I have examined, is almost wholly in the ferric condition. If now we assume that the whole of the iron belongs with the sesquioxide radicals, the analysis would appear as in column 2, and the atomic ratio is then seen to be 2 : 1 : 1 : 1, which is undoubtedly the correct result.

In the year 1851, Mr. W. W. Jefferis, of West Chester, Pa., discovered at the ripidolite locality near that town a peculiar micaceous mineral which exfoliates like the Millbury vermiculite, but which, instead of occurring in small foliæ, is found in large hexagonal plates. This mineral was analyzed by Professor Brush; and although at first referred by him, "with a query," to vermiculite (Am. Jour. Sci., II. xxxi. 369, 1861), was subsequently described as a new species (Am. Jour. Sci., II. xli. 248, 1866), and named Jefferisite.

Several years later, Mr. John Hall, now of Philadelphia, sent to me for examination some rough six-sided prisms of a micaceous mineral, which he had discovered at East Nottingham, in Chester County, Pa. This mineral also exfoliates when heated. It is a new species, and I have named it, after the discoverer, Hallite.

A year since I received from Colonel C. W. Jenks, in connection with other minerals from his corundum mine on the Culsagee River, in Macon County, N. C., a specimen of still another micaceous mineral having the same remarkable pyrognostic properties. It proved to be the best defined of any of this class of minerals which I had examined, and I shall designate it as Culsageeite.

Besides the above, there have been found several other micaceous minerals whose pyrognostic and crystallographic characters indicate that they belong to the same family, but which have not yet been investigated.

The remarkable exfoliation and great apparent increase of volume which the class of mineral under consideration undergo when heated are analogous to the well-known phenomena presented in the dehydration of alum, borax, and other crystalline salts, when heated in a similar way; and it will be one object of this paper to show that the effect is due to the same cause, — namely, to the escaping of what we call water

of crystallization. I also expect to show that the several minerals referred to above are members of a family of hydrous silicates closely allied and parallel to the well-known family of anhydrous silicates called the micas, and that their molecules differ from those of the magnesian micas chiefly in containing a definite number of molecules of water; that is, water of crystallization. I shall call this family of minerals "the vermiculites," using the original name, as "mica" is now employed, to designate a class; and I shall call the three species (or varieties?) of this family Jefferisite, Culsageeite, and Hallite; which correspond, as I expect to show, to the two varieties of Biotite and to Phlogopite respectively. It will appear that the original vermiculite has the same composition as the variety from the Culsagee mine. Finally, attention will also be asked to some unexpected discoveries to which the optical examination of these minerals has led.

Water of Crystallization and Water of Constitution. — In the salts of the stronger acids, the distinction between water of constitution (basic water, as it is sometimes called) and water of crystallization is, as a rule, well marked. Water of crystallization generally escapes at a comparatively low temperature, and the loss is attended with a complete disintegration of the crystals, which usually fall to powder. Water of constitution is held more firmly, and the salt must be heated to a much higher temperature before it is expelled. Moreover, athough the loss of basic water may greatly alter the external aspect of the body, yet there is not the same complete breaking up of the structure as before. To illustrate these points, it is only necessary to refer to the well-known reactions of the common rhombic sodic phosphate when heated.

It is generally believed that the water of crystallization exists as such in the salt, the molecules of water forming a part of the structure of the crystals; and the facts to be presented in this paper tend to support this view. But our modern theories assume that the so-called water of constitution, which may be also driven off when the salt is sufficiently heated, is formed under the influence of the heat from the atoms of hydroxyl $H\text{-}O\text{-}$, which are united to the acid radical of the compound. But in every simple salt, whatever may be our theories in regard to the mode of combination, the weight of the water of constitution, as well as that of the water of crystallization, must bear to the weight of the salt a definite proportion, which can easily be calculated from the symbol; and the ratio between the amount of hydrogen and the amounts of the other radicals must be that of the atomic weights of these radicals or of their multiples. In any given class of salts,

moreover, in which the ratio between the atomicity of the basic and acid radicals has a constant value, all hydrogen, which represents water of constitution, will supplement the other basic radicals, and added to them will complete the relative amount of basic radical which the given class of salts require; while the hydrogen, which represents water of crystallization, will be in excess of that amount.

In mineral silicates these relations are complicated by the phenomena of isomorphous replacements, and, although there may be some question in regard to the replacing capacity of hydrogen, we cannot expect the same constancy in the amount of water of constitution, which these minerals contain, as in the case of simple salts. The amount of water of crystallization, however, must be as invariable in one case as in the other, and the hydrogen must bear the same relations to the atomic ratio of the compound. Thus, if the mineral is an orthosilicate in which the atomic ratio between the *sum of the basic radicals* and the *silicon* is 1 : 1, all hydrogen in excess of the amount which this ratio requires must represent water of crystallization, while all required to complete the ratio must represent water of constitution; and we thus have a means of distinguishing between these two states of combination where the class of compounds to which the mineral belongs is known.

Now, it is true of each of the minerals we have distinguished among the vermiculites, —

First. That the water is driven off at a temperature below a red heat.

Secondly. That the loss of the water is attended with a complete disintegration of the mineral.

Thirdly. That the amount of the basic radicals, exclusive of the hydrogen, is sufficient to saturate the silicon, and that the amount of hydrogen is wholly in excess of the amount which the atomic ratio 1 : 1 requires.

Could it be proved that the vermiculites are orthosilicates, the last of the three facts just stated would be alone sufficient to establish the correctness of our conclusion. Unfortunately such absolute proof cannot be obtained; and we only claim that the crystallographic and chemical relations of the vermiculites to each other, and to the magnesian micas, gives a very high degree of probability to our theory that they are orthosilicates.

From these facts we have concluded that the water which enters into the composition of the vermiculites is water of crystallization. For the evidence of the facts, we refer to the descriptions of the several species given below. But, further, in order to justify our conclusion, we pro-

pose to bring into comparison with the vermiculites a class of hydrous micas from which the water obtained is clearly water of constitution, and this class of minerals we shall first describe.

Damourites. — Delesse originally gave this name to a hydrous mica which occurs in fine scales in Pontivy in Brittany. Since then, micas of similar composition have been observed in several countries, and shown to be not unusual constituents of granitic rocks.* Among these we may distinguish several varieties, (or species?) marked by slight differences of composition and optical characters. But we would propose to give the name Damourite to the whole class, distinguishing the varieties by separate names only so far as may be thought necessary, Under the family of Damourites, then, we class all unisilicate micas, which are chiefly silicates of aluminum and potassium, but in which a portion of the alkaline radical is replaced by hydrogen.

Sterlingite. — A remarkable mineral of the Damourite type is found at Sterling, Mass., associated with spodumene, in a vein of a large bowlder rock. This mineral, for the sake of distinction, I have called Sterlingite; but it does not differ from the original Damourite of Delesse except in the value of the optical angle. We give in parallel columns the characters of the two minerals: —

STERLINGITE.

Mica-like in structure. An aggregate of flexible and unelastic laminæ, frequently an inch in diameter.

Lustre, pearly.

Color, yellow or yellowish-white.

H = 2 — 3.

Sp. gr. at 26°.

1st ex. gave 2.832.

2d „ „ 2.828.

Cleavage basal, highly perfect, as in mica. Jointed parallel to the sides of a rhomb, having an angle of 120°, and also parallel to the shorter diagonal of the same. The markings of these joints, or cleavages, visible on the surfaces of the laminæ.

Double refraction strongly negative.

Biaxial with plane of axes parallel to shorter diagonal. Divergence, about 70°. Dispersion of axes very small.

Before the blowpipe fuses on the edges with potash flame.

DAMOURITE.

Mica-like in structure. An aggregate of fine scales.

Lustre, pearly.

Color, yellow or yellowish-white.

H = 2 — 3.

Sp. gr. = 2.792.

Double refraction negative. Biaxial divergence, 10 to 12 degrees.

* See the papers of Professor Haughton, cited below.

ANALYSIS.

	Sterlingite.	Oxygen.	Damourite. 1.	2.	Oxygen.
SiO_2	43.87	23.40	45.22	43.41	23.15
Al_2O_3	36.45	17.00	37.85	35.17	16.39
Fe_2O_3	3.36	1.00		4.62	1.39
MgO				1.40	0.56
K_2O	10.86	1.84	11.20	10.90	1.85
H_2O	5.19	4.61	5.25	4.50	4.00
	99.73		99.52	100.00	

Of the two analyses of Damourite, No. 1 is by Delesse, of the mineral found in the gangue of cyanite, at Pontivy in Brittany, and No. 2 is by Igelström, of the similar mineral, found at Horrsjöberg, Wermland. The analysis of Sterlingite was made by Mr. C. E. Munroe, Assistant in the Chemical Laboratory of Harvard College, and the above numbers have been abundantly confirmed in repeated analyses by various students in the same laboratory. The alkalies were treated by Smith's process, and the potassium was weighed as PtK_2Cl_6. This value, compared with the total weight of the alkaline chlorides, and that of the chlorine also determined, showed that the alkali in the mineral was almost wholly potash, although the presence of lithium and sodium was plainly indicated by the spectroscope. The water was determined by igniting the mineral in coarse powder, previously dried at 100° C. Even after ignition, the finely pulverized mineral is only partially decomposed by hydrochloric acid, and in the above analysis it was decomposed by fusion with sodic carbonate. The usual tests failed to indicate the presence of fluorine.

Regarding the water as basic, and as forming a part of the protoxides, the atomic ratio in Sterlingite, between the silicon, the sesquioxide radicals, and the protoxide radicals, is

$$\overset{IV}{Si} : \overset{VI}{\text{R}} : \overset{II}{R} = 23.40 : 18 : 6.45, \text{ or nearly } 4 : 3 : 1.$$

The deviation from the simple ratio will not appear so great, as seems at first sight, if it is noticed that a difference of one-half per cent in the amount of water would make the ratio almost exact.

The corresponding ratio in the Damourite from Wermland is

$$23.15 : 17.78 : 6.41, \text{ or, as before, nearly } 4 : 3 : 1.$$

These ratios point to the general formula:—

$$\overset{II}{R}, \overset{VI}{\text{R}} . O_8 . Si_2.$$

The Damourite and Sterlingite are types of a very large class of hydrous micas, which in many places are widely distributed through the granitic rocks. This class of minerals has been especially investigated by Professor Haughton, of Dublin, whose papers may be found in Phil. Mag., IV. ix. 272, and Q. J. G. Soc., xviii. 414, also xx. 280. We cite here a few of his analyses, selected from those given by Professor Dana, — pages 310 and 311, of the fifth edition of his "System of Mineralogy," — in further illustration of the subject we are discussing:

DUBLIN CO. — HAUGHTON. Optical Angle, 58°.

$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{Na}$	$\dot{K}$	$\dot{H}$	
43.47	31.42	4.79	1.13	1.38	1.44	10.71	5.43	= 99.77
23.18	14.64	1.44	0.45	0.39	0.37	1.82	4.83	
23.18	16.09		3.03				4.83	
23.18	16.09		7.86					
3.	2.		1.					

MT. LEINSTER. — HAUGHTON. Optical Angle, 72°.

$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Mg}$	$\dot{K}$	$\dot{H}$	
44.64	30.18	6.35	0.72	12.40	5.32	= 99.61
23.81	14.07	1.90	0.29	2.11	4.73	
23.81	15.97		2.4		4.73	
23.81	15.97		7.13			
3.	2.		1.			

GLENDALOUGH. — HAUGHTON. Optical Angle, 70°.

$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{Na}$	$\dot{K}$	$\dot{H}$	
44.71	31.13	4.69	0.90	1.09	1.27	9.91	6.22	= 99.92
23.84	14.51	1.41	0.36	0.31	0.33	1.68	5.53	
23.84	15.91		2.68				5.53	
23.84	15.91		8.21					
3.	2.		1.					

In these micas again, if we regard the water as basic, we obtain a nearly constant ratio, but differing from that of Damourite in the relation of the two basic radicals. The general symbol of the last would be: —

$$\overset{II}{R}_6, \overset{VI}{R}_4 . O_{36} . Si_9.$$

There appear to be, therefore, these two distinct types of hydrous micas related to the species Muscovite, all rich in alumina and alkali, destitute, or only containing very small amounts, of magnesia, and having a wide optical angle.

The anhydrous Muscovites have not been investigated nearly as fully as the hydrous varieties; and I can find no analyses of any of the beautiful specimens from our American localities. I cite here, for the sake of comparison, an analysis of the Fuchsite, from the Zillerthal, by Schafhäutl (No. 1), and one of a mica, from Fahlun, by H. Rose (No. 2): —

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dddot{Cr}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{Na}$	$\dot{K}$	F	
(1)	47.95	34.45	1.80	3.95	0.71	0.59	0.37	10.75	0.35	= 100.92
	25.57	16.05	.54	1.24	.28	0.17	0.09	1.83		
	25.57		17.83				2.37			

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Mg}$.	$\dot{K}$	$\dot{H}$	F
(2)	46.22	34.52	6.04	2.11	8.22	0.98	1.03
	24.65	16.08	1.81	0.84	1.39	0.87	
	24.65	17.89			3.10		

If now we should add to (1) 6.93 per cent water, and to (2) 3.42 per cent, we should obtain the ratios: —

(1) 25.57 : 17.83 : 8.52, or approx. 3 : 2 : 1,

as in the hydrous micas analyzed by Haughton.

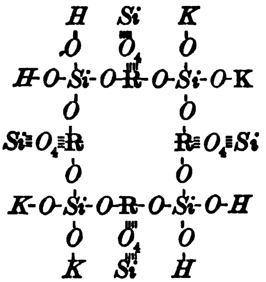
(2) 24.65 : 17.89 : 6.16, or approx. 4 : 3 : 1,

as in Damourite and Sterlingite.

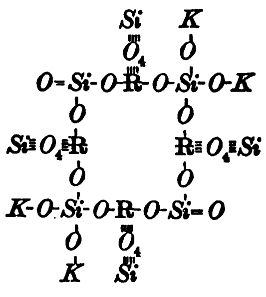
There would seem, then, to be two definite varieties of hydrous micas of the Muscovite family, distinguished by the atomic ratios 3 : 2 : 1 and 4 : 3 : 1. Corresponding to these, it is probable that there are two varieties of anhydrous mica, containing an excess of SiO_2, which, by the addition of sufficient water to saturate the excess of the acid radical, are reduced to one or the other of the two normal types. In a previous paper (Am. Jour. Sci., II. xii. 217, 1867) the author suggested the idea that the excess of silica in this class of micas might result from a mixture of two isomorphous species corresponding to the two hydrates: —

$$H_4{\equiv}O_4{\equiv}Si \text{ and } H_2{=}O_2{=}SiO,$$

and he there described a mica whose atomic ratio was very closely that of the second type, and which he called Cryophyllite. Now, the simplest theory of the relation of the hydrous to the anhydrous Muscovites would seem to be that, while in the molecules of the anhydrous micas a portion of the silicon atoms (the number varying in the different varieties) are in the condition of the first anhydride ($H_2{=}O_2{=}Si\,O$), the hydrous micas contain sufficient basic hydrogen to bring all the silicon atoms into the condition of the normal hydrate ($H_4{\equiv}O_4{\equiv}Si$). The two graphic formulæ which follow indicate, more clearly than any other language can, the relations we have attempted to describe. In these formulæ R stands for the double atom in the radical of the sesquioxides, having the quantivalence of six: —



Hydrous Muscovite.



Anhydrous Muscovite.

The new mineral Sterlingite, whose examination has been the occasion of this discussion, is remarkable as being a very well-defined example of a hydrous mica occurring in large crystals, and exhibiting very marked characters. It does not materially differ in composition from Damourite, and it also agrees with the specimens of this mineral so closely in other physical qualities that we cannot regard the small

optical angle, observed by Descloizeaux on the minute scales of the Pontivy mica, as sufficient ground for separating the new mineral from the old species. We should include under this species all hydrous micas which are rendered by the basic hydrogen orthosilicates, and to it the name Damourite belongs by priority. Sterlingite is simply a variety of Damourite, having the ratio 1 : 3 : 4, with more marked qualities and a wider optical angle than the Pontivy mineral; and, provisionally, the name I have given will be useful in designating it.

The hydrous micas, of which Sterlingite is a variety, have a special interest in connection with the subject of this paper, because they illustrate the characteristics of basic water, which will be contrasted, with those of water of crystallization, in our description of the following species. The evidences that the water in these micas is basic, — that is, forms a part of the basic radical, — may be summed up as follows: —

1. The amount of water in the different varieties is very variable, and bears no constant ratio to that of the other basic radicals.*

2. The hydrogen of the water supplements the other basic radicals and fills out the amount required for a unisilicate, the type to which most of the micas conform.

3. The water is expelled only at a very high temperature.

4. The loss of water is not attended with any marked change in the appearance of the mineral.†

Jefferisite, of *West Chester*. — This well-known mineral, found in the serpentine at West Chester, Pa., was, as I have said, carefully analyzed by Professor Brush, of New Haven, who named it after W. W. Jefferis, Esq., of West Chester; and to this gentleman I am indebted for the specimens of the mineral whose crystallographic relations I have studied. As I am informed by this careful mineralogical observer, the locality is some three miles south of West Chester, where

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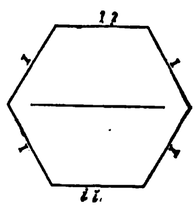
* This fact is not shown so forcibly by the analysis cited above as by the series given by Professor Dana, on pages 310 and 311 of the fifth edition of his "System of Mineralogy," to which we would refer in illustration of this point.

† Since the above was written, we have received from Dr. F. A. Genth his very valuable paper on corundum and its associated minerals. He regards Damourite as one of the most important products of the alteration of corundum, and gives a large number of analyses of specimens from different localities, to which we gladly refer, as they illustrate the point made in this paper, even more markedly than the analyses cited above. The Damourites are evidently widely distributed minerals and characteristic features of certain rocks.

the mineral occurs in several veins or pockets of the serpentine, not more than fifty yards from the quarry where the ripidolite is found. It is associated with oligoclase; and corundum also occurs in the same serpentine formation, in Newton township, ten miles distant, on the north edge of the serpentine ridges. The Jefferisite is found in broad crystals, or crystalline plates, which frequently have a distinct hexagonal form. On two of these plates sent me by Mr. Jefferis, measuring respectively two inches and three-fourths of an inch in diameter, the form is as sharp as on crystals of Muscovite, and the edges make an angle of 120°, as nearly as it can be measured. Mr. Jefferis writes, — "In regard to the Jefferisite crystals which you have examined, the large crystals or plates occurred in the vein immediately under the sod, exposed to all frost, &c.; the small crystals were taken out four or five feet below, in the decomposed Deweylite, and were associated with striated oligoclase, of which I sent you specimens."

The crystals of Jefferisite cleave like mica, affording thin but unelastic foliæ. The cleavage planes are marked triangularly by lines, crossing at angles of 60° and 120°. In some cases there is a jointing as in crystals of mica, parallel to the shorter diagonal of the rhomb. One crystal sent me by Mr. Jefferis is the half of a rough hexagonal prism, an inch and a quarter high by two inches in diameter. The plane of the optical axes, as in the larger number of micas, is parallel to one of these lines, as indicated in Fig. 1, coinciding with the shorter diagonal of the rhombic prism, which appears to be the fundamental form in all this class of minerals, and from which the hexagonal form is derived by the truncation of the two acute angles. The double refraction is strongly negative, but the angle between the optical axes varies in the most remarkable manner. I have measured angles on different plates, of 27°, 24°, and 10°, and observed many intermediate conditions. Owing to the deep yellow color, the plates become opaque at a very moderate thickness, and for this reason it is impossible to measure the angle with great precision. Some of the plates are apparently uniaxial; but this may result from the blending of the two hyperbolas, due to the thinness of the plate. The dispersion of the axes is but slight, and only perceptible in the thicker laminæ when $\varrho < v$. It is obvious, therefore, that the crystallographic characters of the mineral are identical with those of mica.

Fig. 1.



The plates are generally, if not invariably, twinned, and the twin-

ning is the cause of this most remarkable variation in the optical angle, as will be explained at length in connection with our description of Culsageeite. On this last mineral the same phenomena are more marked, owing chiefly to the greater transparency of the plates.

In order to illustrate the chemical relations of the mineral to the Biotite micas, we give below: 1st. The results of the analysis of Jefferisite by Professor Brush. 2d. The same results, calculated for the anhydrous mineral. 3d. The results of an analysis of a Biotite mica, from Pargas, Finland, by Svanberg. In each case I have added the amounts of oxygen in the several oxides, to show the atomic ratios: —

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{K}$	$\dot{H}$	
(1)	37.10	17.57	10.54	1.26	19.65	0.56	0.43	13.76	= 100.87
	19.78	8.18	3.16	.28	7.86	.16	.07	12.23	
	19.78	11.35			8.37			12.23	
	5.	3.			2.			3.	

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\ddot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{K}$	
(2)	42.94	20.33	12.20	1.46	22.75	.66	.50	= 100.84
	22.90	9.47	3.66	.32	9.10	.19	.08	
	22.90	13.13			9.69			
	5.	3.			2.			

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Mn}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{K}$	$\dot{H}$	F	
(3)	42.58	21.68	10.39	.75	10.27	1.04	8.45	3.35	.51	= 99.01
	22.71	10.10	3.12	.17	4.11	.30	1.43	2.98		
	22.71	13.22				8.99				
	5.	3.				2.				

The general symbol of Jefferisite deduced from (1) would be, —

$$\overset{II}{R}_4, \overset{VI}{R}_2 . O_{20} . Si_5 . 6H_2O.$$

A comparison of the results given in (2) and (3) will show that the anhydrous Jefferisite corresponds very closely in its chemical constitution with the Biotite mica from Pargas. The chief difference is to be found in the fact that the mica contains potassium and basic hydrogen, in place of more than one-half of the magnesium of the Jefferisite. It should, however, be remembered in this connection that the Biotites present a very wide variation in the ratio between the amounts of the

protoxide and sesquioxide radicals which the various varieties contain. The limits usually assigned to this variation correspond to the ratios —

$$\overset{\text{II}}{R} : \overset{\text{VI}}{R} : Si = 1 : 2 : 3, \text{ and } \overset{\text{II}}{R} : \overset{\text{VI}}{R} : Si = 1 : 1 : 2,$$

and the Pargas mica with the ratio 2 : 3 : 5 falls between these limits; but the Culsagee variety of vermiculite corresponds to the more common class of Biotites, which have the ratio 1 : 1 : 2.

But this resemblance in chemical constitution only appears when we compare the Biotite mica with the anhydrous Jefferisite; while it is the crystallized hydrous Jefferisite which so closely resembles the magnesian micas in its crystallographic relations; and the question now arises, What is the condition of the large amount of water — 12¼ per cent — which the crystallized mineral contains?

To aid us in forming a conclusion on this point, we have the following evidence:—

First. As the above analysis shows the water is united in definite and atomic proportions amounting to six molecules to every five molecules of silicon in the molecules of the mineral, that is sufficient to convert all the silicon into a hydrate, assuming that the five silicon atoms in this hydrate are joined to each other by the smallest possible number of bonds.

Secondly. While both the crystallographic and the chemical relations of Jefferisite to the other vermiculites, and to the magnesian micas, indicate that the mineral is an orthosilicate, the amount of basic radical, exclusive of the water, is amply sufficient to saturate the atomicity of the silicon.

Thirdly. It was observed by Professor Brush — and his observations have been fully confirmed by ourselves — that the water is given off at a comparatively low temperature, — about 300° C.; and, as every mineralogist knows, this dehydration is attended with that remarkable exfoliation which is characteristic of the vermiculites, and indicates a complete disintegration of the molecular structure. This exfoliation is wholly different from the phenomena which the so-called hydrous micas present under like conditions. In these last — which, as we suppose, contain hydrogen as a part of the basic radical of their molecules — a very high temperature is required to expel the water, and the loss is attended by no such marked change of volume and disintegration.

The conclusion that we draw from these facts is, that the combined water is in the same condition in Jefferisite as in the zeolites, and in many crystallized salts, — a condition which has long been known in chemistry as *water of crystallization.* We shall not here attempt to

discuss what are the relations of the water thus combined to the molecular structure of the mineral. This question is still in suspense, and we are persuaded that our science is not yet in a condition to solve the problem. All that we can at present do is to classify the phenomena presented by the exfoliation of the vermiculite minerals with the efflorescence of Glauber's salt or the intumescence of alum.

If, then, I am justified in the inferences I have drawn, Jefferisite differs chemically from Biotite mica chiefly in containing water of crystallization, very much in the same way that gypsum differs from anhydrite, or common salt from the crystals with two molecules of water, which form in brine at a low temperature. In these bodies, however, the forms of the crystals of the hydrous are wholly different from those of the anhydrous salts, while the crystallographic relations of Jefferisite are very similar, if not identical, with those of the magnesian micas. It is, however, also true that the crystalline structure of the micas seems to admit of a very wide variation of chemical composition. In cryophyllite, which has all the crystallographic characters of the micas strongly developed, is the atomic ratio 3 : 4 : 14; while in the Biotite, whose analysis was cited above, it is 2 : 3 : 5. The first is an acid, and the last a neutral silicate. The other varieties of mica have a composition intermediate between these extremes; and it might be said, if such a variation of composition is compatible with the crystalline structure exhibited by this group of minerals, it would not be surprising if the structure were sufficiently elastic to admit of the insertion of the water of crystallization without great alteration of external form.

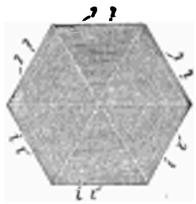
It may be further urged that the normal mica crystal (a rhombic prism with angles of 60° and 120°) is a form which appears to be related to a mode of molecular structure common to a great many substances, and the phenomena which will be described in this paper seem to sustain this opinion. Still, we do not care to theorize about the subject. Our object is simply to make prominent the two points: 1st. That the crystallographic structure of Jefferisite is identical with that of the magnesian micas. 2d. That the chemical constitution of the anhydrous mineral is closely allied to that of Biotite.

Culsageeite or the Vermiculite of the Jenks Mine, North Carolina.— Through the kindness of Colonel C. W. Jenks, the proprietor of the corundum mines on the Culsagee River in Macon County, N. C., I have had an opportunity of examining a variety of vermiculite which at that locality forms an important part of the matrix of the corundum. The associations of the mineral in North Carolina are very similar to those

in Pennsylvania. Professor J. Lawrence Smith, in his recent article in Am. Jour. Sci. (III. vi. 180), says that "in the development in North Carolina the corundum" (with which the vermiculite is associated) "occurs in chrysolite or serpentine rocks, and outside of serpentine it has not been found. These chrysolite rocks belong to a regular system of dikes which have been traversed for the distance of about one hundred and ninety miles. This system of dikes lies on the north-west side of the Blue Ridge, and has a strike parallel to the main mass of the ridge, and has an average distance from the summit of the ridge of about ten miles. The serpentine appears at intervals along this whole line of one hundred and ninety miles," and "is usually enclosed in a hard crystalline gneiss." In the serpentine the corundum has been found at several localities along a distance of forty miles. Colonel Jenks writes me: "The workmen have opened a new vein they call the gem vein. It is walled with chrysolite, and the fissure is from one to four feet wide, which fissure is filled with ripidolite, and in this the corundum crystals are imbedded." As regards the association of the ripidolite and vermiculite, he also writes: "They occur both alone and intermingled and also in layers, like the leaves of a book." Again: "The ripidolite maintains a uniform character of texture and appearance, whether associated with the vermiculite or alone. In the vein at the bottom of the shaft I have spoke of, and elsewhere, it is of uniform hardness, texture, &c., but in it the corundum seems to have lost cohesion, — in some localities falling to pieces, and crumbling out of the ripidolite matrix. But, when exposed to the air and sunshine for a day or two, the corundum regains its cohesion, and you can then chip off the ripidolite from it. It is just the opposite with the vermiculite when alone the matrix. Sometimes it occurs in masses, several feet long, formed of scales as large as your hand, easily separating like mica from the corundum, which in this matrix always seems to retain its cohesion. Then, again, the vermiculite will occur in masses of many bushels, all broken up and disintegrated, like very coarse bran, in which the crystals of corundum lie like eggs in a box of sawdust. The great crystal (weighing 316 pounds) was thus deposited. At other places the entire mass seems to have changed to the color of white Castile soap, with specks of green in it, the corundum crystals all falling apart until exposed, when they harden." This untechnical language of an unprofessional but accurate observer conveys a very vivid idea of the mode of association of these minerals. The specimens so kindly sent me by Colonel Jenks confirmed in all respects his observations. In several cases the corundum was still imbedded in both the ripidolite and the

vermiculite, and the scales of these minerals not unfrequently penetrated the corundum crystals in such a way as to indicate that the corundum had crystallized around them. The ripidolite is firm in texture, and closely resembles the variety from West Chester. It occurs in hexagonal plates, which have a striation similar to that I formerly described as characteristic of the Pennsylvania specimens (Am. Jour. Sci., II. xliv. 201, 1867), and which is illustrated by Fig. 2. Professor Smith, *loc. cit.*, gives analyses of two varieties of ripidolite — one compact, the other friable — as follows:—

Fig. 2.



COMPACT RIPIDOLITE FROM NORTH CAROLINA.

$\ddot{\mathrm{Si}}$	$\dddot{\mathrm{Al}}$	$\dddot{\mathrm{Fe}}$	$\dot{\mathrm{Mg}}$	$\dot{\mathrm{H}}$	
27.00	21.60	16.63	22.00	12.30	= 99.53

FRIABLE RIPIDOLITE FROM NORTH CAROLINA.

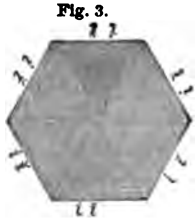
$\ddot{\mathrm{Si}}$	$\dddot{\mathrm{Al}}$	$\dddot{\mathrm{Fe}}$	$\dot{\mathrm{Mg}}$	$\dot{\mathrm{H}}$	
29.15	10.50	23.50	25.44	10.04	= 98.63

A determination of the silica in the compact mineral made by Mr. F. Gooch, student in the Laboratory of Harvard College, gave 27.25 per cent of SiO_2, and 11.93 H_2O, as a mean of two closely agreeing determinations. But in the specimens sent me by Colonel Jenks I did not recognize the friable variety.

The vermiculite occurs in close contact with the ripidolite, and is frequently interlaminated with it, *but the two are always perfectly distinct*, thus entirely disproving the theory that the vermiculite was derived from the ripidolite by weathering. It occurs in large plates having more or less of an hexagonal outline. Some of those received from Colonel Jenks were five inches in diameter. It has a greenish-yellow color, which is very much lighter than that of the West Chester variety. The plates are strongly marked by lines crossing at angles of 60° and 120°, like those from West Chester; but these lines are more marked in the North Carolina variety. This variety is also much more friable than the other, and readily breaks in directions parallel to these lines,—yielding rhombic plates with angles of 120° and 60°, and more readily hexagonal or triangular plates, produced by the truncation of the 60° angle of the rhombic plate, on a line parallel to the shorter diagonal of the fundamental rhomb. The plates most readily break

parallel to this diagonal, and, like the specimens from West Chester, are frequently jointed in this direction. Like other micaceous minerals, the plates cleave readily parallel to the basal plane, yielding very thin foliæ, exceedingly flexible, but not elastic. The optical characters are the same as those of the West Chester variety, — strong negative double refraction yielding a biaxial ring system, with uniform distribution of colors, and very variable optical angle. I have measured angles from about 30° to about 13°. The angle often varies widely in different parts of the same plate. Thus I have measured on different laminæ, from a single plate not exceeding 3 inches in diameter, the three angles 30°, 24°, and 13°; and again I have noticed a similar variation on one and the same lamina. Indeed, the phenomena which I observed were almost identical with those I had previously observed on plates of ripidolite from Texas, Pennsylvania, *loc. cit.* On moving the lamina just referred to parallel to itself, in front of the polarizing microscope, the optical angle varied as I passed from one side of the field to the other. Beginning with a value of about 30°, the angle decreased to about 13°. Moving the plate still further, I found a region of indistinctness, and then the axes opened again, — the new plane making an angle of 120° to the old. I had evidently here a macling precisely similar to that I had previously described in the Texas ripidolite, and shown in Fig. 3, where the lines of shading represent the position of the plane of the optical axes. This represents what we may call an ideal macle; for I have seldom been able to trace more than three individuals on the same plate, and, as a rule, these are very unequally developed. On many of the specimens of the North Carolina vermiculite, the macling is externally marked by the eminent cleavage or jointing parallel to the shorter diagonal of the rhomb section, and in several of the specimens I have examined it was quite symmetrical. A study of these specimens led me to an explanation of the cause of the remarkable variation of the optical angle, which I believe not only applies to the vermiculites and ripidolites, but also, in many cases at least, to the micas. It would be expected that the several members of such macles as Fig. 3 represents would penetrate each other, and I therefore made a series of experiments to ascertain what would be the effect of the interfoliation of laminæ in which the planes of the two sets of optical axes had the same relative position as in the several members of the macle. To that end I divided a plate, which presented the largest optical angle I had observed, into as thin laminæ as possible, and then superimposed them in the relative

Fig. 3.



position I have mentioned, so that the planes of the optical axes should be inclined at an angle of 60°. The result was — when the thickness of the plates in each position were nearly equal — that a symmetrical ring system was obtained, in which the optical angle was about 13°, — the smallest I had measured; and, by varying the relative thickness, intermediate degrees of optical divergence were produced. By now introducing laminæ into the compound crystal, in the position of the third member of the macle, — that is, with the plane of the optical axes in the position of the third diagonal of the hexagon, — the apparent angle could be reduced still further, so that the plate was apparently uniaxial. Although these experiments were sufficient to show that the macling was an adequate explanation of the apparent variation of optical angle I had observed in the plates of ripidolite and Jefferisite, they also raised the question how far the effect I had obtained in my experiments might be due to the circumstance, that, on account of the deep color of these minerals, it is only possible to experiment on very thin plates, with which, of course, the rings of interference are very wide, and the hyperbolas proportionally indefinite. I therefore next made a similar experiment with a well-known phlogopite mica from Jefferson County, N. Y., whose crystals are very distinctly macled after the type of Fig. 3 or 5, the plates presenting a variation of optical angle similar to that I have described, the normal axial divergence being about 15½°. A very clear portion of one of these plates was first cut into a regular hexagon, one of whose diagonals was in the plane of the optical axes. This hexagonal plate was then split into twelve laminæ, which were superimposed with the intervention of balsam, and in alternating positions, like the members of a macle, — the optical plane in each of the laminæ making an angle of 60° with that of the lamina above or beneath it. The result was an essentially uniaxial plate, differing from a plate of uniaxial mica only in small irregularities in the contour of the rings, such as the lamination would be expected to produce. On repeating now this experiment with a Muscovite mica having a wide optical angle about 63°, I obtained a most remarkable and unexpected result, — a structure presenting optical phenomena similar to those of a plate of quartz cut perpendicularly to the principal axis. At the first trial I obtained a compound mica plate showing a disk of color in the centre of the field whose tint changed during the rotation of the analyzer, — of the polarizing microscope, — like a plate of left-handed quartz; and, on superposing a plate of right-handed quartz, the spirals of Airy at once appeared. The rings, however, were wholly broken up, and appeared only in irregular

patches of color. This irregularity was due to the unequal thickness of the laminæ employed, and I found it impossible to split up one and the same hexagonal plate of mica into laminæ, which were sufficiently uniform for the purpose. But very satisfactory results were obtained in the following way. I selected for the purpose the very clear and easily cleavable mica from Grafton, N. H.; and, after a few trials, succeeded in cleaving off very thin plates of considerable size and nearly uniform thickness. Selecting one of these plates, I first divided it by means of a parallel ruler into strips, and from these strips cut out the hexagonal laminæ by means of a steel pattern carefully made. The thin mica can be cut with perfect accuracy by a sharp knife on a plate of glass. The hexagonal laminæ thus obtained, though coming from different parts of the mica plate, were optically parallel to each other; and by drawing at the outset a line, with a sharp point, near the corresponding edges of the several strips, this line served as a guide for placing the hexagonal laminæ. From laminæ thus prepared, plates were made showing the familiar system of rings as perfectly as could be expected. The best results were obtained with plates consisting of from twelve to twenty-four laminæ; and the character of the resulting plate, whether left or right handed, was found to depend on the order of the spiral arrangement. If in building up the pile the marked side of each successive lamina is turned through an angle of 60° in the direction of the motion of the hands of a watch, the result corresponds to left-handed quartz if turned in the reverse direction to right-handed, and on superposing two dissimilar plates thus prepared I obtained again the spirals of Airy in great perfection. Thus, then, it appears that, even with micas of the widest optical angle, we can build up a structure which is optically uniaxial.*

* The great difficulty in preparing these plates is to obtain thin films of mica of uniform thickness, which are of sufficient size to yield a dozen or more laminæ; and the more nearly we have succeeded in preparing such a film, by splitting sheets of mica, the more closely we have been able to imitate the phenomena seen under like conditions with a plate of quartz. We have been able to work with films which measured with a spherometer only $\frac{1}{400}$ of an inch in thickness, and have not obtained good results with those which were much thicker, and when thinner than this the mica cannot readily be cut into shape. The least inequality in the thickness of the several laminæ composing the same plate more or less mars the effect; and, although some of the striking features seen with quartz may remain, such as the succession of colors on revolving the analyzer, and even the spirals of Airy, yet the more delicate phases of the phenomena disappear. The plate changes color when revolved in its own plane, the rings lose their circular form and become confused, and the violet cross disappears. Moreover, as regards the conditions which determine the phase of the circular polarization, the law stated above can only be affirmed with cer-

The theory which I have formed to account for these facts is as follows. We may conceive that the molecule of mica is an ellipsoid, whose elliptical section, through the longer axis, can be inscribed in the rhomb of 60° and 120°. Assume now that these molecules have polarity, the rhombic prism would be the normal result of their association, as represented in Fig. 4. We may, however, conceive that three of these molecules may become associated by alternate single poles to form a nucleus, such as represented in Fig. 5. Such a group once formed would be in a condition of great stability, resulting from the concurrent action of the several poles; and if now each of the molecules develops into a crystal, the result would be a macle of a form which is very common in the mineral kingdom. If six molecules unite in a similar way to form a nucleus, as in Fig. 6, we should also have stable equilibrium (although less firm than before), and the result of a symmetrical development would be a macle such as has been represented in Figs. 2 and 3. Whether this more complex arrangement is necessary in order to explain the phenomena presented by

Fig. 4.

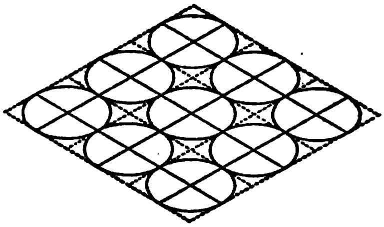
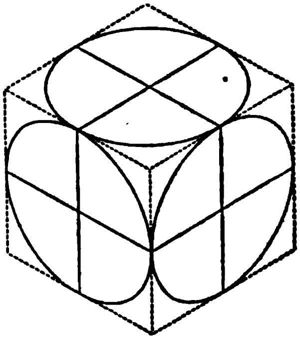


Fig. 5.

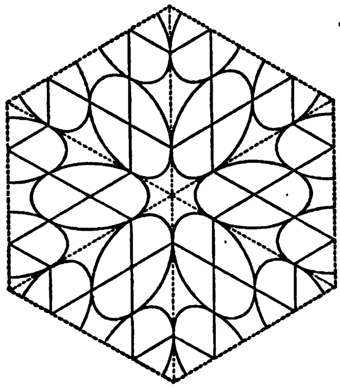


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tainty of plates consisting of laminæ which very nearly fulfil the conditions we have described. Very small inequalities of thickness renders the effect irregular, and made it at first difficult to discover the law. Our experiments have been a series of approximations; and, although we may never be able with our rude appliances to compete with nature in the manufacture of uniaxial crystals, yet we have approached so near to the perfect result as to be able to point out with confidence one way, at least, by which the effects seen in natural crystals may be produced. We have usually cut the laminæ into regular hexagons, but equilateral triangles might more easily be cut, and would probably give as good results; for, although the errors of position might not be so well distributed, we have found that a slight variation in the relative position of the laminæ injures the result to a far less degree than the least inequality in their thickness. It still remains to make careful quantitative measurements of the effeots produced under determinate conditions; and, as can easily be seen, the subject opens a wide field for mathematical analysis as well as physical investigation.

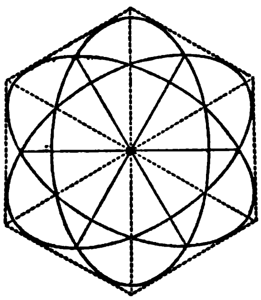
the vermiculites and micas, I do not feel confident. It is seldom that more than three individuals can be distinguished on a given plate; and the very unequal development of the several individuals, and the indefiniteness of the lines of demarcation, resulting from the phenomena which have been described, render what would seem to be a characteristic feature of the more complex group not necessarily a certain indication of the structure. I refer to the fact, very constantly noticed, that the plane of the optical axes is parallel to the nearest hexagonal edge, as shown in Figs. 2 and 3. In Figs. 5 and 6 this same plane is parallel to the shorter axis of the ellipse; and it can easily be seen that if either of the individual of Fig. 5 were developed over any large portion of the space of its neighbors, the optical plane might appear parallel to the adjacent edge.

Fig. 6.



Having made the two suppositions, as above, to explain the phenomena of twinning, which have been long familiar and externally visible, it will not, we trust, appear unreasonable if we make a third supposition to explain the phenomena first described in this paper. We may conceive that the ellipsoidal molecules, instead of grouping together on the same plane, become associated by their alternate poles, one over the other, as represented in Fig. 7. Molecules so associated, developing laterally, would produce the laminæ of a mica plate in the relative position in which we have placed them in our artificial crystals, with only this difference, that the laminæ would be indefinitely thin, and in exact position; and the effect of such compound molecules in modifying the elasticity of the crystalline structure must be, in most respects at least, like that of single molecules, symmetrical on all sides of one line or axis,—in other words, they must produce a structure similar to that of uniaxial crystals. Under what further conditions the grouping of

Fig. 7.



the molecules, in right or left handed spirals, determines the phenomena of right or left handed circular polarization, and what bearing the new facts may have on the received theory of these phenomena as they appear in quartz, must be left for further analysis to discuss.

I pass next to consider the composition of the Culsagee vermiculite, and I give below, at (1), (2), and (3), the results of three analyses, made by myself, together with the corresponding oxygen ratios.

The pulverized mineral, after it has been exfoliated by heat, is easily and perfectly decomposed by hydrochloric acid. In analysis (1), after the separation of the silica, the alumina and ferric oxide were separated from the magnesia by ammonia, with the usual precautions. In (2) and (3) the bases were converted into nitrates and separated by Deville's method. In each case the magnesia was weighed as pyrophosphate, and the alumina and ferric oxide were weighed together.

All three analyses were made with material rendered anhydrous by ignition until the weight was constant, and each is represented by three distinct determinations; namely, the weight of the silica, the sum of the weight of the alumina and ferric oxide, and the weight of the magnesic pyrophosphate. The oxides of iron and the water were once for all determined on separate portions of the dried but not exfoliated mineral, and therefore appear of the same value in all the analyses.

The determination of the water was the only difficulty which the analysis of this mineral presented. It is by far the most hygroscopic silicate I have ever examined, when once dry absorbing water from comparatively dry air with almost as much avidity as chloride of calcium. In two experiments with different portions of the same powder, the material was heated in an air bath, at 100° C., for seventy-two hours before the weight became constant; and in each case the weight was compared at intervals of about six hours. The total loss in the first experiment was 10.27 per cent, and in the second 10.19 per cent. The mineral thus dried lost when ignited 10.84 per cent. Another portion of the same powder, which had been dried over sulphuric acid for more than two months, lost when ignited 11.09 per cent. This close agreement indicates that all the water lost in drying, either at 100° or over sulphuric acid, is hygroscopic; and the conclusion is confirmed very greatly by the fact that the mineral in thus drying does not change its aspect in the least degree, and rapidly reabsorbs the water when exposed to the air. On the other hand, when the mineral is ignited it swells up to many times its volume, like other members of the vermiculite family, and undergoes what is evidently a profound alteration in its molecular structure.*

* In his valuable paper on corundum, above referred to (p. 44), Dr. Genth

	Si	Al	Fe	Fe	Mg	H	
(1)	37.58	19.73	5.95	0.58	25.13	11.09	= 100.06
	20.04	9.19	1.78	0.14	10.05	9.86	
	20.04	10.97		10.19		9.86	
	2.03	1.11		1.03		1.	
(2)	37.43	19.75	5.95	0.58	25.58	11.09	= 100.38
	19.96	9.20	1.78	0.14	10.23	9.86	
	19.96	10.98		10.37		9.86	
	2.03	1.11		1.05		1.	
(3)	37.10	20.22	5.95	0.58	25.07	11.09	= 100.01
	19.79	9.42	1.78	0.14	10.03	9.86	
	19.79	11.20		10.17		9.86	
	2.	1.13		1.03		1.	

has published two analyses of the Culsagee vermiculite, made in his laboratory by Mr. Chatard and Dr. Koenig. Their results agree very closely with those given above, except in the amount of water; and since, as Dr. Genth states, the analyses were made with material which had been dried *in vacuo* over sulphuric acid for only four days, it is obvious that they have estimated as combined water a large portion of what we, for reasons stated, have regarded as hygroscopic moisture. Reducing their results to the same standard as our own, the close agreement becomes evident. We give, for comparison, first the results, as published; second, the same reduced to a water percentage of 11%; third, the corresponding oxygen or atomic ratios.

	Si	Al	Fe	Fe	Ni	Mg	H	
Mr. Chatard.	33.93	17.88	5.42	0.50	0.85	23.48	19.17	= 100.18
	37.83	19.12	5.94	0.55	0.38	25.77	11.09	
	19.91	8.91	1.78	0.12	0.07	10.81	9.86	
	19.91	10.69			10.50		9.86	
	2.02	1.06			1.05		1.	
Dr. Koenig.	33.77	17.56	5.61	0.50		22.48	20.80	= 100.22
	37.65	19.58	6.26	0.56		25.06	11.09	
	20.08	9.12	1.88	0.12		10.02	9.86	
	20.08	11.00			10.14		9.86	
	2.04	1.11			1.08		1.	

The close agreement of these results with our own, obtained by different processes and with different specimens of the mineral, indicates a remarkable constancy of composition for a micaceous mineral. I have confirmed Dr. Genth's observation of the presence of a very small amount of nickel in the mineral, and I also detected in it a trace of copper.

It is evident from these analyses that the atomic ratio of the mineral is 2 : 1 : 1 : 1, and its formula may therefore be written: —

$$R_3, \text{R} . O_{12} . Si_3 . 3H_2O.$$

By referring to what has already been said of the relation of Jefferisite to the Biotites, it will be seen that, while that mineral corresponds to a less common variety of this species, the Culsagee vermiculite corresponds to its more usual type. We give below, at (1), the results of an analysis of Vesuvian Biotite, by Chodnef; and, at (2), the same, assuming that a portion of the iron is in the ferrous condition, as is well known to be the case, in order to show that values within the probable error of the analysis would give the ratio 2 : 1 : 1. Here, of course, the alkali takes the place of a portion of the magnesia of the vermiculite.

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{K}$
(1)	40.91	17.19	11.03		19.04	0.30	9.96 = 98.43
(2)	40.91	17.19	7.03	4.00	19.04	0.30	9.96 = 98.43
	21.82	8.30	2.11	.89	7.62	0.09	1.69
	21.82	10.41			10.29		
	2.12	1.01			1.		

This new variety of vermiculite is so well marked, and the composition so definite, that I have thought best to designate it by the name Culsageeite. As regards its other characters, it has a specific gravity of 2.225 (taken in alcohol), and about the hardness of talc. Before the blowpipe the exfoliated mineral fuses readily to a white enamel, but does not fuse in the flame of a Bunsen lamp.

To this variety of vermiculite belongs, as I have already intimated, the original mineral from Millbury, analyzed by Crossley. There can be no question as to the general accuracy of Crossley's results; and, assuming that all the iron is in the ferric condition, they give, as I have shown, almost precisely the atomic ratio 2 : 1 : 1 : 1. The only question that can arise is in regard to the condition of the iron. I have therefore made an assay of the iron by the accurate method I formerly described in the Am. Jour. Sci., xliv. 347, 1867. One hundred parts of the massive mineral gave 7.40 per cent ferric oxide, and 3.86 per cent ferric oxide, which corresponds to a total of 10.56 ferrous oxide. Crossley found 10.02 ferrous oxide, but he separated with great care the vermiculite from the steatite with which it is mixed; and this steatite was probably the source of the greater part of the small quantity of ferrous oxide found in our assay, which, though not made with

pure material, shows conclusively that the condition of the iron in the Millbury vermiculite is not different from that in other varieties of the same family of minerals.

Hallite. — Several years since this variety of vermiculite was sent to me by Mr. John Hall, of Philadelphia, by whom it was originally discovered. The examination then made showing that the mineral was a new variety, if not a new species, of the vermiculite family, I gave to it the name of Hallite, in recognition of the mineralogical services of Mr. Hall, who not only discovered the mineral, but has carefully worked the locality and observed the associations in which it is there found. A preliminary notice of the mineral under this name was published at the time by Professor Leeds, of Hoboken; but the interesting relations which the mineral bears to the subject of this paper have made a further examination desirable.

Hallite occurs in large rough six-sided prisms, with easy micaceous cleavage. There are two varieties, differing markedly in color, green and yellow; and I am indebted to Mr. Hall for the following facts in regard to the locality and associations of this species. Mr. Hall writes: "The mineral is found at East Nottingham, in the serpentine formation of south-eastern Pennsylvania, three miles south of Oxford, in Chester County; and I know of no other locality. I think the green and yellow varieties are very closely related, and may possibly pass from one into the other; but I have no positive proof that they do. The crystals are found in nests or pockets, and the two colors are not found in the same nests. The green crystals are imbedded in a steatite earth or base of the same color as the crystals, and the yellow in a yellow earth; and sometimes nests, containing the opposite varieties, are only a few feet apart in seams of the serpentine rock."

As the following analyses show, the two varieties have essentially the same composition, and the only difference that could be detected was in the degree of oxidation of the iron. The yellow crystals appeared to be more weathered than the green, and on the last the green color frequently fades out towards the centre of crystals, thus giving indications of a metamorphosis by which one variety may pass into the other.

Under the microscope these scales of the mineral show a remarkable appearance. Between the greenish or nearly colorless plates are seen elongated scales of a yellow mineral resembling closely in color thin scales of Jefferisite. They are more or less spear-shaped in form, although usually very narrow, and lie accurately in parallel lines, which cross at angles of 60° and 120°, like the magnetic oxide of iron in the Muscovite from Pennsbury, Pa., or the microscopic crystals in the

Biotite of South Burgess of Canada; and the phenomenon of asterism, seen so beautiful with the plates of the last, can also be seen with thin laminæ of Hallite. It was impossible to free the mineral from this admixture, but specimens were selected for analysis as free from it as possible. It was also impossible to determine its exact nature. The scales had not a definite form, but there was a tendency to a rhombic shape, which is well described by the term "spear-shaped;" and though the material is so widely distributed through the crystal, the total mass must be very small.

This mineral is not so hygroscopic as Jefferisite, and no difficulty was found in drying the material for analysis. When ignited, it exfoliates like other species of vermiculite, but not nearly to so great an extent as Jefferisite. After ignition it is decomposed by hydrochloric acid. The specific gravity of the green variety, mean of four determinations, 2.398; that of the yellow variety, mean of two determinations, 2.402. Before the blowpipe fuses with difficulty to a brown enamel. The following analyses were made by Mr. C. E. Munroe, Assistant in the Laboratory of Harvard College:—

GREEN VARIETY OF HALLITE.

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\dot{K}$	$\dot{H}$	
(1)	35.97	7.61	8.83	1.13	31.34	0.43	14.32	= 99.63
(2)	35.80	7.29	8.73	1.13	31.56	0.49	14.33	= 99.33
(Mean.)	35.89	7.45	8.78	1.13	31.45	0.46	14.33	= 99.49
	19.14	3.47	2.63	0.25	12.58	0.08	12.74	
	19.14	6.10			12.91		12.74	
	3.	0.96			2.02		2.	
	3.	1.			2.		2.	

YELLOW VARIETY OF HALLITE.

	$\ddot{Si}$	$\dddot{Al}$	$\dddot{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\dot{K}$	$\dot{H}$	
(1)	35.17	7.74	9.76	0.32	31.61	0.56	14.65	= 99.81
(2)	35.34	7.42	9.61	0.32	31.41	0.65	14.91	= 99.66
(Mean.)	35.26	7.58	9.68	0.32	31.51	0.61	14.78	= 99.74*
	18.81	3.53	2.90	0.10	12.60	0.10	13.14	
	18.81	6.43			12.80		13.14	
	3.	1.03			2.04		2.09	
	3.	1.			2.		2.	

$$R_{12}, \mathbf{R}_2 \,.\, O_{36} \,.\, Si_9 \,.\, 12H_2O.$$

* Trace of manganese.

It will be seen from the above analyses that, although the atomic ratio between all the basic radicals and the silicon is the same as in Culsageeite, Jefferisite, and Biotite, the ratio between the protoxide and sesquioxide radicals is very different. In this respect the mineral resembles the phlogopite micas, in which also the protoxide radicals preponderate; and the symbol given above for Hallite, less the water, is identical with that given by Professor Dana as the more probable formula of the phlogopites.

The opacity produced by the interspersed material made it difficult to determine the optical characters of the mineral, as the rings produced with polarized light could only be seen with very thin plates, and the cross was therefore ill defined; so that, although in some cases there appeared to be a separation of the hyperbolas, the plates could not be distinguished from uniaxial. On one specimen the hexagonal form was very perfect, and the crystal presented the planes of a rhombohedron having an angle over the basal edge of about 122°, resembling the crystals of Biotite from Greenwood Furnace. Mr. Hall informs me that these more perfect crystals have only been found in one pocket of the serpentine.

The distinction, however, between the phlogopites and the biotites is not fundamental, either chemically or physically. Chemically, both species are orthosilicates; that is, the atomic ratio between the silicon and the sum of the basic radicals is 1 : 1. The species differ in composition only in the relative proportion of the sesquioxide and protoxide radicals. In the phlogopite the ratio of $\overset{\text{II}}{R}$ to $\overset{\text{VI}}{\mathbf{R}}$ is probably normally 2 : 1; but of the published analyses the value varies between that ratio and the ratio 3 : 2. In the biotites the same ratio is probably normally 1 : 1; but here, again, the different analyses which have been made give values varying between 5 : 3 and 1 : 2. In like manner the optical distinction between the phlogopites and biotites, of which so much has been made, is equally indefinite. Between a so-called phlogopite, like that from Jefferson County, N. Y., with an angle of about 15°, and the apparently uniaxial plates of biotite from Vesuvius, there is every possible gradation — sometimes, as I have shown, on one and the same mica plate; and I have endeavored in this paper to explain the cause of this variation. With the Vesuvian biotites themselves, — if the specimens in the mineralogical cabinet of Harvard College are fair representatives of the mineral from this locality, — it is only occasionally that we find a perfectly uniaxial plate. More commonly there are distinct evidences of twinning, and on the borders of the hexagonal plate may be dis-

covered a biaxial structure of which the optical plane is parallel to different edges of the hexagon on different parts of the plate.

It must, however, be remembered that, as by the process of twinning we have described the structure of the magnesian micas approaches that of uniaxial crystals, rhombohedral and other planes characteristic of the hexagonal system begin to appear on the crystal. This is illustrated not only by the crystals of Biotite from Vesuvius and from Greenwood Furnace, N. Y., but also by the more perfect crystals of Hallite from Chester County, Pa. In other words, *the process of twinning we have illustrated in this paper produces hexagonal crystals in external form as well as in optical characters;* and the question naturally arises, May not the hexagonal crystals of other minerals be formed in a similar way? — that, is, may they not be developed from twinned molecules, which, though in their aggregate producing an hexagonal structure, singly would develop into biaxial crystals? Bearing on this point, we have discovered some very remarkable evidence.

We have in our possession a plate of Elba tourmaline cut perpendicular to the axis, in which the polarizing microscope shows on different zones a separation of the hyperbolas, which amounts in some positions to eight degrees; and in moving the plate across the field the optical divergence varies precisely as on plates of phlogopite and vermiculite. There is certainly no external evidence of lamination on tourmaline crystals, for the mineral is remarkably compact, and the crystals have not even a basal cleavage: but it will be remembered how readily some of the varieties pass by alteration into micas of the magnesian type; and this change to a foliated structure, in which the lamination is parallel to the base of the original hexagonal crystal, may be facilitated by a grouping of the molecules of the tourmaline, in the manner represented by Fig. 7.

We have also a plate of amethystine quartz, in which a beam of parallel polarized rays of light exhibits a twinning almost as symmetrical as that shown in Fig. 5, — the three zones being most beautifully mapped out by the alternating bands of right and left handed quartz, which are such a familiar phenomenon of these crystals; but, besides this, in each of these zones, near the border of the plate, can be distinguished a biaxial structure with an optical divergence of several degrees; and, on one other plate of amethyst we have had an opportunity of examining, we have also seen under the polarizing microscope the biaxial curves at one or more points.

These facts most distinctly suggest the theory that the optical phenomena of quartz are produced by a molecular structure similar to that

by which we have obtained identical phenomena in our artificial plates of mica, and that the two orders of crystals are aggregates of compound molecules, whose parts are twinned together in the one case in right-handed, and in the other in left-handed spirals, and, lastly, that the simple molecule, if developed normally, would produce a biaxial structure.* This theory is most markedly in harmony with the chemical relations of silica. The compound SiO_2 is the only one of the tetrad oxides which crystallizes in the hexagonal system; and ever since, by the study of the organic compounds of silicon, the quadrivalent character of the element has been made evident, this fact has been a striking anomaly in our chemical classification. Assume, however, that the molecule SiO_2 would develop normally into a rhombic structure, and that the hexagonal form of quartz is solely a result of molecular twinning, and the anomaly disappears. The molecule SiO_2 may be approximately of the same form as the molecule TiO_2, in Brookite; but, having the exact dimensions and polar conditions which favor the mode of molecular twinning, described above and represented by Fig. 7, it may always develop into hexagonal shapes.

Are, then, all hexagonal forms thus closely related to the rhombic systems of crystals? And do all molecules of the dimensions and polar conditions illustrated by the figures of this article — that is, those which correspond to the rhomb of 60° and 120° — usually develop into hexagonal forms? May not the whole difference between an hexagonal and a rhombic form arise from a slight difference of dimensions, which determines a molecular macling in the one case, and a normal development of the single molecules in the other? These questions point out most interesting lines of investigation, and will recall to the mineralogist a number of facts bearing upon the subject. Allow me to refer to two of the most striking and most obvious.

On the crystals of chrysoberyl, the rhombic angle is 119° 46′; and every mineralogist is familiar with the hexagonal macling, similar

* Since the above was in type, we have received Am. Jour. Sci., IV., February, 1874, containing a description of the rhombic silica which Professor Maskelyne, of the British Museum, has discovered in the meteorite of Breitenbach. This new species of silica, which Professor Maskelyne calls Asmanite, has the form of a right rhombic prism, with an angle of 120° 20′, and the crystals are optically biaxial; but while the specific gravity of quartz is 2.6, that of Asmanite is said to be 2.245. It is perhaps to be expected that such a molecular macling as we have described would determine an increase of density, since thereby three molecules coalesce to form one; or it is possible that the remarks made in regard to calcite beyond apply also to quartz; but still the marked difference remains to be explained.

to Fig. 2, which is so very characteristic of this species.* Corundum differs chemically from chrysoberyl, in that a portion of the alumina in the former is replaced by glucina in the latter. Corundum has a perfect hexagonal form, and, fundamentally, may not the only crystallographic difference be that, in consequence of the replacement, a rhomb of 120° changes to a rhomb of 119° 46′? Now we have a plate of macled chrysoberyl, showing the normal wide divergence of the optical axes at certain points on its borders, and a nearly uniaxial structure at the centre, where there is an obvious interpenetration between the individuals of the macle, and where the superposition of the several laminæ is most beautifully shown by a polarized beam of parallel rays. We have also a section of a corundum crystal, presenting phenomena similar to those seen with the plate of tourmaline, described above. Further, we have observed like phenomena on a section of phenacite; and, although the last mineral contains silica, yet if the molecules of SiO_2 are crystallographically equivalent to those of Al_2O_3, it may be that the molecular structure both of phenacite and of beryl is more closely allied to that of chrysoberyl and corundum than the received theory of their chemical constitution would indicate.

We would not convey the impression that in all these crystals the appearances we have described are strongly marked, or that they have passed wholly unnoticed hitherto. Every one who has become familiar with the optical properties of crystals must have noticed that, with many always regarded as uniaxial, there is not unfrequently in some positions a small separation of the cross into the hyperbolas, which are characteristic of biaxial structure. But these irregularities, although long known, have never been satisfactorily explained. They have been hitherto residual features not accounted for by the received theory of crystalline structure, which explains so satisfactorily the general order of the phenomena observed with the polariscope. We have endeavored in this paper to trace their true significance: first, by showing that the appearances we are discussing are precisely similar to the effects which can be obtained by known means with mica plates; and, secondly, by observing on different specimens of various minerals every intermediate stage between the unmistakable effects of twinning on plates of mica or vermiculite, and the delicate phases of the same phenomena, seen with sections of crystals of tourmaline, corundum, or phenacite. One other illustration of our theory.

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* See also Dana's System of Min., 5th ed., Figs. 154, 155, p. 156.

The rhombic angle of witherite (native baric carbonate) is 118° 30′, and the all but universal hexagonal macling of crystals of this species is a well-known fact.* The rhombic angle of aragonite (the corresponding form of calcic carbonate) is 116° 10′, and the much greater divergence of this angle from 120° determines, as is also known, a style of macling which is usually quite different from that of witherite. In the isomeric calcite, however, we have the type of all hexagonal forms. Hitherto the crystalline forms of calcite and aragonite have been regarded as being as widely separated as possible, and a comparison of these two well-known mineral species has furnished one of the most striking illustrations of demorphism. But may not, after all, the comparatively small physical differences between these two minerals correspond to a crystallographic difference no greater, fundamentally, than the difference between the rhomb of 116° 10′ and the rhomb of 120° ?

The macles of chrysoberyl and witherite are illustration of a general truth, fully recognized in mineralogy, that all rhombic crystals, whose angles approach 120°, tend to form hexagonal macles. The optical phenomena described in this paper certainly suggest the theory that a perfect hexagonal form and structure may be the result of a more fundamental and molecular macling, which results when the angle is exactly 120°.

Observations of Senarmont.—The only previous observations which we have been able to find bearing on the subject of this paper are those of the late eminent mineralogist, H. de Senarmont, of Paris. In a well-known paper (Ann. Chim. et Phys. 3ˢ xxxiii. 391), Senarmont showed that salts which were both geometrically and chemically isomorphous might have very different optical relations; for example, that, while the biaxial crystals of two such salts might have the same bisectrix, the plane of the optical axes in the crystals of one might be perpendicular to the corresponding plane in those of the other. He further proved, by crystallizing together two salts so related, that in the crystals of the isomorphous mixtures thus obtained the optical angle varied with the varying proportions of the constituents, between the extreme conditions in the crystals of either salt; and by trial he succeeded in forming from two biaxial salts crystals which, in monochromatic light at least, appeared uniaxial. In a later paper (Ann. Chim. et Phys. 3ˢ xxxiv. 171), Senarmont applied the principles, which he had thus experimentally verified, to explain the variation of the optical angle of the micas. In this paper he seeks to prove, first,

* See figures, Dana's System of Min., p. 697.

that all micas may be referred to a right rhombic prism with angles of approximately 60° and 120°; secondly, that, while in some micas the plane of the optical axes is parallel to the shorter diagonal of the rhomb, as in Fig. 8, in others it is parallel to the longer diagonal, as in Fig. 9. Interpreting these facts by the results of his experiments on isomorphous salts, he draws the inference that there are, crystallographically at least, but two species of mica which are geometrically isomorphous but optically distinct, that these are represented by the varieties which have the widest optical angle between the axes in either plane, and that all other varieties with optical angles varying from 0° to 70° in either direction are isomorphous mixtures of the two optically distinct conditions of the mineral.

Fig. 8.

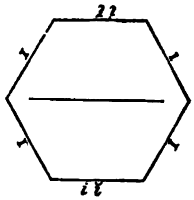
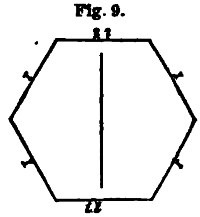


Fig. 9.



The observations described in this paper, although they prove that another cause may also determine the variation of optical angle in micaceous minerals, do not necessarily invalidate this beautiful theory of Senarmont. The variations observed with other minerals, not only on different specimens, but with the same specimen at different temperatures, and which are so beautiful seen with the orthoclase from Wehr in the Eifel, and with crystals of selenite, indicate that such variations may be determined by conditions of molecular structure wholly independent of the macling here described. We have shown that the macling does produce the variation in certain cases, and it must remain for future investigation to assign the limits of the influence which this cause may exert. We would only remark in conclusion that, although in the 57 varieties of micas examined by Senarmont he did not note a single instance in which the position of the plane of the optical axes — with reference to the diagonal of the rhomb — was different on different parts of the same specimen, or even on different specimens from the same locality, he does describe and figure several remarkable macles of muscovite mica similar to those of vermiculite described above and represented by Fig. 5. In one instance the plane of the optical axes is parallel to the shorter, and in the other to the longer diagonal of the rhombic prism; but in both cases it has the same relative position in the several individuals of the macles, the three planes forming with each other angles of 60°. On the plate of another macle a difference of optical angle was observed on different portions of the plate, and this effect was probably similar to that we

have been studying in this paper. On another plate, from the same crystals he observed a superposition of the laminæ of the different individuals of the macle; and the following language by which this phenomena is described, and which is the only reference made to it, shows how closely he came to the results recorded in this paper: —

"Une partie seulement du cristal maclé est commune aux trois lames; mais ici certaines plages (pointillées sur la figure) ont un caractère optique tout particulier; elles ne cessent jamais de développer des couleurs dans la lumière polarisée, quelle que soit d'ailleurs l'orientation de la lame cristallisée. Il est évident que dans ces plages il y a superposition de lames appartenant à des cristaux orientés, les uns comme le petit, les autres comme le grand cristal, de façon que quand les unes ont leurs sections principales dans le plan de polarisation, les sections principales des autres font avec ce plan des angles de 60 degrés.

"Cet exemple prouve donc, non-seulement que les micas peuvent se grouper latéralement sans que leurs clivages cessent d'être parallèles, mais que des feuillets superposés peuvent même appartenir à des cristaux dont l'orientation diffère de 60 degrés. Un pareil mode de groupement, qui ne trouble ni la régularité de la cristallisation, ni la transparence, semble indiquer que l'arrangement moléculaire de ces prismes rhomboïdaux diffère très-peu de celui qui conviendrait au prisme hexagonal régulier."

XVIII.

MELANOSIDERITE:

A NEW MINERAL SPECIES, FROM MINERAL HILL, DELAWARE COUNTY, PENNSYLVANIA.

BY JOSIAH P. COOKE, JR.

Read, May 11, 1875.

FOR the specimens of this mineral I am indebted to Mr. W. W. Jefferis, of West Chester, Pa., who informs me that the locality is not over 500 yards from the Hallite locality (see these Proceedings, Vol. IX., page 59), lying a little off from the serpentine range in a bed of clay.

The mineral is compact and amorphous. It is very brittle, and its fracture is conchoidal. Hardness about 4½. Sp. Gr., in two determinations (made with alcohol, but referred to water), was 3.390 and 3.392. Lustre, vitreous inclining to resinous. Color, black, with a tinge of red. Streak, brownish red to brick red. Subtranslucent; and, in thin plates, cherry red by transmitted light. Heated before the blowpipe in a closed tube, it decrepitates and gives off water. In the forceps it fuses at about 4½ to an iron-gray mass, which is strongly attracted by the magnet. On platinum wire with soda, it dissolves with effervescence. With borax glass it gives the reactions for iron. The powder dissolves very readily in muriatic acid; but, as soon as the amount added exceeds a certain limit, the solution gelatinizes.

In the following analysis, the water was determined by ignition; the iron and alumina were weighed together, and the amount of iron in the ignited precipitate determined by titration. The silica was separated and weighed in the usual way.

	1	2	3	Average.	Atomic Ratio.	Theory Requires.
SiO_2	7.39	7.45		7.42	49	7.42
Fe_2O_3	75.13			75.13	3.07	79.21
Al_2O_3	4.34			4.34		
H_2O at 100°	6.17	13.85	13.79	13.83	1.54	13.37
H_2O above 100°	7.68					
				100.72		100.00

The last column gives the percentage corresponding to the symbol $\ddot{\bar{F}}e_4 \ddot{S}i \dot{H}_6$; and it is obvious that the composition of the mineral is remarkably definite, and the agreement of the analyses with theory very close.

Melanosiderite is closely related to the sesqui-hydrates of iron. If the silica could be regarded as an impurity, the ratio between the sesquioxide and the water would be precisely that of Limonite; and, on the other hand, if we regard the basic radical as neutralized both by the silicon and the hydrogen, then the ratio would be that of Göthite. Melanosiderite differs, however, most markedly from both of these minerals in its specific gravity.

	Sp. Gr.	
Göthite	4. — 4.4	Dana's Mineralogy.
Limonite	3.6 — 4.	„ „
Melanosiderite	3.391	As above.

Moreover its vitreous lustre, its fusibility, its definite composition, and, above all, its reaction with acids (gelatinizing), indicate that it is a true silicate. The mineral which it most closely resembles, both in external appearance and specific characters, is Hisingerite, but this contains thirty-six per cent of silica. Melanosiderite, however, is evidently a highly basic compound of the same class; and the new species has a special interest, arising from the circumstance that it is a definite natural example of a class of compounds which are so characteristic of the ferric radical. Its amorphous colloidal structure is wholly in accordance with this view of its constitution. The name Melanosiderite is derived from Greek μέλας and σίδηρος, and refers to the very striking black color of the mineral.

The analytical work in this investigation has been done by Mr. W. H. Melville, of the Senior Class in Harvard College.

XIX.

ON TWO NEW VARIETIES OF VERMICULITES,

WITH A REVISION OF THE OTHER MEMBERS OF THIS GROUP.

By Josiah P. Cooke, Jr.,
Erving Professor of Chemistry and Mineralogy at Harvard College,
AND
F. A. Gooch,
Assistant in the Chemical Laboratory.

Presented, May 11, 1875.

Since the publication of the writer's first monograph on the vermiculites,* two new varieties of this group of minerals have been brought to his notice by Mr. W. W. Jefferis, of West Chester, Pa., who has most kindly furnished the materials for the following investigation.

The first of these varieties — which occurs at Lerni, Delaware Co., Pa. — has the following characters: The unaltered mineral is of a dull sea-green color, has a highly developed micaceous structure, is an aggregate of rough hexagonal plates, and of very imperfect external form. It is transparent in moderately thin laminæ, and is free from enclosed foreign matter. The optical characters of the mineral closely resemble those of the Culsagee variety of vermiculite, the angle between the optical axes varying in different parts of the same laminæ from 18° to 0°. Its hardness is about 1.5, and three determinations of its specific gravity (taken in alcohol at 23° C.) gave 2.409, 2.368, and 2.373. Heated in a closed tube, it gives off water acid in reaction, changes color, and doubles its volume. Heated before the blowpipe, it fuses to a dirty enamel.

The mineral was prepared for analysis by drying at 100° until its weight was constant, and in this condition was easily decomposed by hydrochloric acid. The bases, after the separation of silica, were con-

* The Vermiculites, their Crystallographic and Chemical Relations to the Micas, by Josiah P. Cooke, Jr. These Proceedings, vol. ix. p. 85. The analytical work in this second paper has been done by Mr. Gooch.

verted into nitrates, and separated by Deville's process. The iron and alumina were weighed together as oxides, and the magnesia as the pyrophosphate. The amount and condition of the iron were determined by decomposing the mineral by the process described by the writer in Am. Jour., vol. xliv. page 347, estimating by a standard solution of potassic permanganate the ferrous iron at once, and the total amount of iron after reduction to the ferrous state. Small amounts of lithium and potassium were found by the spectroscope in the residue obtained in Smith's process for the determination of alkalies, but the total amount of alkali probably did not exceed one-tenth of one per cent of the mineral. The mineral, dried at 100°, lost upon ignition,

(1.)	(2.)	(3.)	(Mean.)
11.65	11.67	11.71	11.68

per cent of its weight. The details of these determinations will be referred to hereafter. Taking, then, 11.68 as the percentage of water in the mineral, the results of analysis are as follows: —

	(1.)	(2.)	(3.)	(Mean.)	Ratio.
$\ddot{Si}$	38.17	37.93	38.00	38.03	2.54
$\overset{\cdots}{\bar{Al}}$	12.84	13.07	12.87	12.93	.75
$\overset{\cdots}{\bar{Fe}}$	7.02	7.02	7.02	7.02	.26
$\dot{Fe}$	.50	.50	.50	.50	.01
$\dot{Mg}$	——	29.72	29.57	29.64	1.48
$\dot{\bar{Li}}$, $\dot{\bar{K}}$	——	trace	....	....	
$\dot{\bar{H}}$		11.68	11.68	11.68	1.30
		99.92	99.64	99.80	

$\ddot{Si}$	:	$\overset{vi}{R} + \overset{ii}{R}$	:	$\dot{\bar{H}}$		$\overset{vi}{R}$	:	$\overset{ii}{R}$
2.54	:	2.50	:	1.30		1.01	:	1.49
2	:	2	:	1		2	:	3

The second of these two varieties of vermiculite occurs at Pelham, Mass. It has a greenish-yellow tint, resembling closely in color the Culsagee variety. In the specimen examined, however, the scales were very much smaller than those of the Culsagee variety, and exhibited no regular outline. Examined with the microscope, they appeared equally free from interpenetrating material. The plates do not show the striation observed both in Culsageeite and Jefferisite. No evidence of macling could be found. The plates were optically biaxial,

with a small optical angle and strong negative double refraction like the other vermiculites and magnesian micas. The hardness of the mineral is about 1.5; two determinations of its specific gravity (taken in alcohol at 22° C.) gave 2.160 and 2.161. Heated in a closed tube, it gives off water acid in reaction, changes color, and doubles its volume, and in the forceps before the blowpipe fuses to a dirty enamel.

The mineral, dried at 100°, lost upon ignition

(1.)	(2.)	(3.)	(4.)	(Mean.)
11.21	11.50	11.13	11.43	11.32

per cent of its weight. The details of these determinations will be referred to hereafter.

In (1), (2), (3), and (4) of the following analyses, the ignited mineral was decomposed by fusion with sodic carbonate; in (5) and (6), the mineral, dried at 100°, was decomposed by hydrochloric acid. In all, the ferric and aluminic oxides were weighed together, and the former subsequently determined by reduction and titration with a solution of potassic bichromate. In (4), the iron and alumina were together separated from magnesia by precipitation by ammonia, with the usual precautions. In (5), the bases were converted into nitrates, and alumina and iron separated from magnesia by Deville's process. In both (4) and (5), the magnesia was weighed as the pyrophosphate. A trace only of ferrous iron was found. The spectroscope indicated small amounts of lithium and potassium.*

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
$\ddot{\mathrm{Si}}$	41.14	41.28	41.04	40.78	41.27	41.23
$\bar{\mathrm{Fe}}$		4.35	4.26	4.49	4.14	
$\bar{\mathrm{Al}}$		} 43.25	43.52	15.05	15.19	
$\dot{\mathrm{Mg}}$		}		28.82	28.25	
$\dot{\bar{\mathrm{Li}}}$, $\dot{\bar{\mathrm{K}}}$ trace	. . . . .	. . . . .	. . . . .	. . . . .	. . . . .	. . . . .
$\dot{\bar{\mathrm{H}}}$	11.32	11.32	11.32	11.32	11.32	
		100.20	100.14	100.46	100.17	

Analysis (5), which probably represents the amount of magnesia contained in the mineral more correctly than (4), affords the ratio,

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* In Hallite and Jefferisite, as well as in the Lerni and Pelham varieties, small amounts of lithium were detected. In none of the vermiculites have we been able to detect fluorine.

	$\ddot{Si}$	:	$\bar{Al}$	:	$\bar{Fe}$	:	$\dot{Mg}$	:	$\dot{H}$
	2.75	:	.88	:	.17	:	1.41	:	1.26
	2.75	:	1.05			:	1.41	:	1.26
or	2.75	:			2.46			:	1.26
approximately	9	:			8			:	4

The writer has described (loc. cit.) the remarkable hygroscopic properties of the vermiculites, and the difficulty of separating the constitutional from the hygroscopic water which they may contain. The varieties from Lerni and Pelham offer the same difficulty in the determination of their water, thirty to forty hours being required to bring one or two grammes of either of them to a constant weight at 100° C.

In obtaining a constant temperature of 100° C., an electric regulator was used which differs from other similar forms of apparatus in simplicity of construction. The current is made or broken by a very slight rise or fall of mercury in a U tube connected with a glass bulb within the air-bath. By means of a pressure tap which closes an open L of the connecting tube, the air within the bulb may be confined as soon as the bath reaches the required temperature. After this a very slight increase of temperature raises the mercury column sufficiently to close the electric circuit, and then the current shuts the cock which regulates the supply of gas to the burner under the bath. The chief advantage and the novelty of the apparatus is to be found in the simplicity of this stop-cock, which was suggested by Professor H. B. Hill. It consists of an ordinary chloride of calcium tube placed horizontally, and closed at the larger end by a rubber stopper which allows a considerable freedom of motion to a smaller glass tube passing through it; by this the illuminating gas enters the chloride of calcium tube, from which it passes to the burner. When the current is closed, an electro-magnet acting on an armature attached to the outer end of the small tube plunges the curved inner end beneath the surface of some mercury in the bulb of the chloride of calcium tube, and thus shuts off the main supply of gas; although a small orifice in the side of the inner tube allows a sufficient flow to keep the flame under the air-bath alive. The variation of the temperature of the air-bath does not ordinarily exceed one or two degrees during periods of fifteen to twenty hours, even under great variations of pressure in the gas mains.

Table I. shows the percentages of water found in air-dried specimens

of the Lerni vermiculite, and Table II. shows the percentages of water found in the same specimens dried at 100° C.

I.

	(1.)	(2.)
Loss at 100° C.	5.75	8.12
" about 300° C.	10.97	
" red heat . . .	. . . . . .	8.60
	16.72	16.72

II.

	(1.)	(2.)	(3.)	(Mean.)
Loss at about 300° . .	11.65	2.54	11.71	
" red heat . . .		9.13		
	11.65	11.67	11.71	11.68

Table III. gives the percentages of water found in air-dried specimens of the Pelham vermiculite, and Table IV. gives the percentages of water found in the same specimens dried at 100° C.

III.

	(1.)	(2.)	(3.)	(4.)
Loss at 100° C.	10.83	10.72		10.80
" about 300° C.	4.35	10.27		10.14
" red heat	5.65			
	20.83	20.99		20.94

IV.

	(1.)	(2.)	(3)	(4.)	(Mean.)
Loss at about 300° . . .	4.90	11.50	11.13	11.43	
" red heat . . .	6.31				
	11.21	11.50	11.13	11.43	11.32

The marked hygroscopic character of the Culsagee, Lerni, and Pelham vermiculites led to the idea that the discrepancies between the published analyses of Jefferisite and Hallite might be due to the hygroscopic nature of these minerals. The water contained in each of them was therefore carefully again determined. Table V. gives the percentages of water found in air-dried specimens of Jefferisite; analyses (1), (2) and (4) of Table VI. give the percentages of water found in the same specimens dried at 100°; (3 *a*) gives the percentages of

water found in the mineral dried for three months over sulphuric acid, and (3 *b*) the percentages found in the same specimen subsequently dried at 100° C.

V.

	(1.)	(2.)	(3.)	(4.)
Loss at 100° C.	10.28	9.66		10.17
„ about 300 C. }	9.58	{ 4.24 }		9.36
„ red heat }		{ 5.43 }		
	19.86	19.33		19.53

VI.

	(1.)	(2.)	(3 *a*.)	(3 *b*.)	(4.)
Loss at about 300° C. }	10.47	{ 4.70	4.46	4.31 }	10.42
„ red heat }		{ 6.01	6.20	6.14 }	
	10.47	10.71	10.66	10.45	10.42

The mean of (1), (2), (3 *b*), and (4) of Table VI. is 10.51.

It would appear from analysis (3) that the amounts of water lost at 100° C. and over sulphuric acid, during a period of three months, are very nearly identical. Assuming that 10.51 (the mean of the four determinations above) represents the percentage of water in the mineral, dried at 100°, the following scheme contains the published analyses of Jefferisite reduced to this basis. Analyses (1), (2), and (3) are those of Prof. Brush, Dr. Koenig, and Mr. Thomas M. Chatard respectively: —

	Si	$\overline{Al}$	$\overline{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\dot{Ca}$	$\dot{K}$	$\dot{H}$	Total.
(1.)	38.47	18.24	10.92	1.31	20.38	.56	.45	10.51	100.89
Ratio	2.56	1.06	.34	.04	1.02	.02	.01	1.17	
		1.40			1.09				
	2.56	:		2.49			:	1.17	
(2.)	37.25	19.87	8.17	2.36	21.51	—	—	10.51	99.67
Ratio	2.48	1.16	.31	.06	1.07			1.17	
		1.47		1.13					
	2.48	:		2.60		:		1.17	

(3.)	38.04	18.39	8.84	2.33	21.34	—	—	10.51	99.45
Ratio	2.56	1.07	.33	.06	1.07			1.17	

Ratio: 1.07 + .33 → 1.40; .06 + 1.07 → 1.13; 1.40 + 1.13 → 2.53

2.56 : 2.53 : 1.17

Table VII. gives the percentages of water found in air-dried specimens of the green variety of Hallite, and Table VIII. gives the percentages of water found in the same specimens dried at 100°. In analysis (4) the mineral was dried for three months over sulphuric acid, and when subsequently heated to 100° for twelve hours met with no appreciable loss.

VII.

	(1.)	(2.)	(3.)	(4.)	(Mean.)
Loss at 100°	3.48	3.19	2.86	2.85	
„ about 300°	12.38 (about 300° and red heat)	12.86 (about 300° and red heat)	2.03	2.28	
„ red heat			10.77	10.55	
	15.86	16.05	15.66	15.68	15.81

VIII.

	(1.)	(2.)	(3.)	(4.)
Loss at about 300°	12.82 (about 300° and red heat)	13.29 (about 300° and red heat)	2.09	2.44
„ red heat			11.09	10.77
	12.83	13.29	13.18	13.21

The mean of (2), (3), and (4), which agree closely, is 13.23. Reducing therefore Mr. C. E. Munroe's analysis of this same variety to this basis, the following scheme represents the constitution of the mineral dried at 100°.

	$\ddot{Si}$	$\overline{Al}$	$\overline{Fe}$	$\dot{Fe}$	$\dot{Mg}$	$\overline{K}$	$\overline{H}$	
	36.34	7.54	8.89	1.14	31.84	.47	13.23	99.45
Ratio	2.42	.44	.33	.03	1.59	.01	1.47	

Ratio: .44 + .33 → .77; .03 + 1.59 + .01 → 1.63; .77 + 1.63 → 2.40

2.42 : 2.40 : 1.47

It will be noticed, however, that in the case of Hallite there appears to be a constant condition of hydration at about 300°, and that in two experiments the air-dried mineral lost above this temperature 10.77 and

10.55 per cent of its weight. The mean of these values is 10.66; and regarding this as the water of crystallization of the mineral, and reducing Mr. Munroe's analyses accordingly, we obtain the following results: —

$\ddot{\text{Si}}$	$\bar{\text{Al}}$	$\bar{\text{Fe}}$	$\dot{\text{Fe}}$	$\dot{\text{Mg}}$	$\dot{\text{K}}$	$\dot{\text{H}}$
37.17	7.72	9.06	1.18	32.57	.48	11.24
2.48	.45	.34	.03	1.62	.01	1.25
	.79			1.66		
2.48	:		2.45		:	1.25

It would appear, then, that Hallite at 300° is in the same condition of hydration which the other vermiculites examined assume at or about 100°. Now, corresponding to this, there is a very marked fact, indicated by the tables given above, which is worthy of special notice. Air-dried Jefferisite loses, at 100°, about ten per cent of its weight, while air-dried Hallite loses only about three per cent, showing that it holds its water much more firmly than the first. In order to institute a just comparison between the different vermiculites, it is obviously important to seek for each variety the point at which the mineral assumes a constant condition, and maintains it through a considerable variation of temperature. Save only some practical convenience, there is no peculiar virtue in 100°, as the temperature at which a mineral should be dried for analysis. As in the case of crystalline salts we should expect to find for each hydrous mineral a certain point or points of temperature at which it loses the whole, or a part, of its water of crystallization, and certain limits between which it maintains a constant composition. Moreover we should expect that these temperatures would be the more definite in proportion as what we may call the hygroscopic power is the more marked; that, while in some cases the mineral would lose its water at a nearly constant temperature, and the intervals of definite hydration would be well marked, in others the loss would extend over a considerable range of temperature, and it would be more difficult to secure the states of definite composition. That such differences as these are conspicuous among the vermiculites the tables given above abundantly show; but, in addition to this evidence, the difference in the behavior of the several varieties, when heated, impressed upon us more strongly the principle we have stated than the figures would indicate. Nevertheless, as the following table shows, we have been able to bring all the vermiculites to essentially the same

condition. The table is merely a summing up of the results already given, and exhibits a comparison of the atomic ratios * of the several varieties.

	IV. Si.		VI. II. R + R.		II. H.	VI. R.		II. R.
Hallite, at about 300° C.	2.49	:	2.47	:	1.25	.77		1.63
	2	:	2	:	1	1	:	2
Pelham Vermiculite, at 100°	2.75	:	2.46	:	1.23	1.05	:	1.43
	2	:	2	:	1	2	:	3
Lerni „ „ „	2.54	:	2.50	:	1.30	1.01	:	1.49
	2	:	2	:	1	2	:	3
Culsagee „ „ „	2.50	:	2.66	:	1.23	1.37	:	1.27
	2	:	2	:	1	1	:	1
Millbury „ (Crossley)	2.38	:	2.74	:	1.14	1.37	:	1.37
	2	:	2	:	1	1	:	1
Jefferisite „ at 100°	2.56	:	2.53	:	1.17	1.40	:	1.13
	2	:	2	:	1	3	:	2

In the next table we bring together some further noteworthy results, of which the details have already been given, indicating that in the case of three, at least, of the vermiculites we have evidence of different degrees of hydration corresponding to different temperatures: —

	IV. Si.	VI. II. R + R.	II H.				
Atomic Ratio of Hallite Air-dried	2.35 :	2.34 :	1.76	or	8 :	8 :	6
„ „ „ at 100°	2.42 :	2.41 :	1.47	or	8 :	8 :	5
„ „ „ at 300°	2.48 :	2.45 :	1.25	or	8 :	8 :	4
Atomic Ratio of Pelhamite Air-dried	2.45 :	2.19 :	2.32	or	4 :	4 :	4
„ „ „ at 100°	2.75 :	2.46 :	1.26	or	4 :	4 :	2
„ „ „ at 300°	2.90 :	2 59 :	.74	or	4 :	4 :	1
Atomic Ratio of Jefferisite Air-dried	2.30 :	2.28 :	2.17	or	4 :	4 :	4
„ „ „ at 100°	2.56 :	2.53 :	1.17	or	4 :	4 :	2
„ „ „ at 300°	2.68 :	2.65 :	.70	or	4 :	4 :	1

* The atomic ratio is the same ratio which in most works on Mineralogy is still called the oxygen ratio. The numbers given in this paper are found by dividing the per cent of each oxide by a divisor, which is the quotient of the molecular weight of the oxide divided by the quantivalence of the radical. See writer's Chemical Philosophy, page 450, or Paper on Atomic Ratios, Am. Jour., vol. xlvii., May, 1869.

In the last two varieties the ratios correspond to the symbols: —

$$\overset{\text{VIII.}}{Si_2}\ \overset{\text{VIII.}}{O_8}\ \overset{\text{VIII.}}{(\bar{R}, R)} \ .\ 4H_2O$$

$$\text{do.} \qquad .\ 2H_2O$$

$$\text{do.} \qquad .\ H_2O.$$

Here again it will be noticed that the differences in the definiteness of these ratios correspond to the differences of hygroscopic power described above. In the case of Hallite, the ratios are almost precisely those of even molecules, while in the case of Jefferisite the agreement is much less close.

In conclusion, we consider that the following general results may be deduced from this investigation: —

First. That all the vermiculites are unisilicates.

Secondly. That these minerals combine with water in several definite proportions, thus confirming the opinion advanced by the writer in his previous paper on this subject, that the water in the vermiculites is water of crystallization.

Thirdly. That all these minerals may be reduced to the condition expressed by the ratio 2 : 2 : 1, which we regard as the normal ratio of the vermiculites.

Fourthly. That the only essential difference between the different varieties of vermiculites is in the ratio between the sesquioxide and protoxide bases.

ABSOLUTE SYSTEM OF ELECTRICAL MEASUREMENTS.

By Josiah P. Cooke, Jr.

1. *Introduction.*—The great improvements in the methods of electrical measurement, which have been made within a few years, and to which the success of ocean telegraphy is chiefly due, we owe, in no inconsiderable measure, to the labors of the Committee on Electrical Standards of the British Association for the Advancement of Science. This committee, composed of the most eminent electricians of England, have not only constructed an absolute standard of resistance (the Ohm), but they have also, by their public influence and individual investigations, very greatly promoted the recent rapid advance of electrical science. Since the new units of the Association are rapidly coming into universal use, and as no detailed account of the new system is readily accessible to American students it has been thought that the following analysis of the subject would be acceptable to the readers of this *Journal.* The following pages have been compiled chiefly from the Report of the British Association for 1863. A knowledge of the elements of electricity is assumed and the well-known laws of electrical currents are made the basis of the demonstrations which follow.

Electro-magnetic System.

2. *Ohm's law.*

$$C=\frac{E}{R}, \qquad [1.]$$

where C = strength of current.
E = electro-motive force.
R = resistance.

These elements should be referred to such standards that the unit electro-motive force must produce the unit current in a circuit of unit resistance. Otherwise we should be obliged to introduce into all calculations, some useless and absurd factor.

3. *Faraday's law.*

$$Q=C\,t, \qquad [2.]$$

where Q = quantity of electricity.
t = time (in seconds) during which current flows.

Hence the unit of quantity must be that quantity of electricity which is conveyed by the unit current in the unit of time.

4. *Joule's law.*

$$W=C^2\,R\,t, \qquad [3.]$$

The work done by a current (*e. g.* in generating heat) is proportional to the square of the current, to the resistance of the circuit and to the time during which it acts.

The heat generated by a current of known *strength* in flowing through a known *resistance* during a known *time* can be accurately measured. The mechanical equivalent of heat is well known. The unit of heat being taken as the amount of heat which will raise 1 gramme of water from 0° to 1° C., the mechanical equivalent of this unit is 4157·25 absolute units of work, or 423·8 metre-grammes.*

Hence this equation gives us the means of connecting directly the system of electrical measures with the fundamental units of time, space and weight. In order to make our electrical measurements consistent with the metrical system, we should choose our units such that the unit current in flowing through the unit resistance, should do work equivalent to the unit of work in one second. The units of C and R must then be so taken that $t \times R \times C^2$ shall always give the value of the work done in metrical units. This, however, is consistent with various units, only if either of the two is chosen arbitrarily, the other is fixed by the condition given. Further, when the units of R and C are fixed, the unit of E is also fixed by [1].

Corollary.—By substituting in [3] $Q = C\,t$, and then $\frac{E}{R} = C$ (from [1] and [2]) we easily deduce.

$$W = Q\,E, \qquad . \quad . \quad . \quad . \quad . \quad . \quad [4]$$

that is, the work done is measured by the quantity of electricity multiplied by its fall in tension. Hence, in our system, the unit quantity falling in tension the unit of electro-motive force will do the metrical unit of work.

5. *Magnetic Law.*—It is well known that an electric current exerts a force on the pole of a magnet in its neighborhood. This effect is a purely mechanical phenomenon, and must be measured by the ordinary mechanical units. The unit of force is that force which imparts to one gramme of matter the velocity of one metre in one second. The force exerted by a current on a magnetic pole has been found to be:

(1) Proportional to the strength of current, or C.

(2) Proportional to the strength of pole, or *m*.

* The absolute unit of work is the unit of force acting through one metre. The force of gravity acting on one gramme of matter exerts 9·8 units of force. Hence one metre-gramme equals 9·8 units of work.

And if the conductor be at all points equidistant from the pole, or in other words, be bent in a circle with a radius, K, the force is also

(3) Proportional to the length of conductor, L.

(4) Inversely proportional to the square of the radius, K^2.

Moreover, it is affected by no other quantities. Hence we have,

$$F = \frac{C L m}{K^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad [5]$$

Here L and K are lengths in metres; m, or the strength of magnetic pole, is measured by reference to the unit magnetic pole, which is the pole that, at a distance of one metre, repels a similar and equal pole with the unit force. F is measured in units of force defined as above.

Thus, by this equation, the value of C may be referred directly to the fundamental mechanical units. The unit current must be that which, in a unit length, produces the unit force on a unit pole at the unit distance, and this unit is called the *electro-magnetic absolute unit.*

Corollary.—We may easily bring [5] into a form in which it is more useful. One pole of a magnet can never practically be separated from its opposite; and we must next consider the action of a current on a magnetic needle. In order to make the conditions as simple as possible, we will assume that the needle is very short, and in all its motion is enclosed within a coil of conducting wire. A current flowing through such a coil creates within the coil a magnetic field.* The directions of force † in this field are all parallel to the axis of the coil, and the intensity ‡ of the field is uniform throughout the whole space within the coil. We will further assume that the coil is placed in the magnetic meridian, and that a current passing through the coil deviates the needle from the meridian by an angle, d. It is easy to see that the forces acting on the two poles, and tending to turn the needle, would be as above, each equal to $F = \frac{C L m}{K^2}$.

* A magnetic field is any space in the neighborhood of a magnet.

† The direction of the force at any point of a magnetic field, is the direction in which a pole would be urged, or which a magnetic needle would take if suspended at that point.

‡ The intensity of the field, at any point, is measured by the force which the unit pole would experience at that point.

These two forces would form a couple acting with a leverage equal to one-half the length of the needle, so long as the needle remains in the meridian. Hence the effect of the couple would be represented by $\frac{\text{C L } m\, l}{k_2}$, where $m\, l$ represents the magnetic moment.

When deflected to an angle d the force would act as strongly as ever, but the effect of the couple on the needle would be diminished because the moment is not now $m\, l$, but $m\, l$ cos. d.



The strength of the couple now, is therefore—

$$\frac{\text{C L } m\, l}{k_2} \cos. d.$$

When the needle comes to equilibrium the effect of this couple is exactly balanced by a second couple created by the earth's magnetism. The space in which our experiments are made is a magnetic field of uniform intensity, the directions of the forces in that field are sensibly parallel, and the intensity of that field is capable of measurement. The directions of the lines of force are shown by a dipping needle, but as a magnetic needle is usually hung so that it can only move in a horizontal plane, it is usual to estimate only the horizontal force of the earth's magnetism, which we will represent by H.* The effect of the earth's magnetism on a pole would be m H, and the effect of the magnetic couple on our needle when pointing E—W, would be H $m\, l$, while the effect of the same couple on the needle making an angle d with the meridian would be H $m\, l$ sin. d. But since the magnetism of the earth is assumed to just balance the magnetic couple, we have—

$$\frac{\text{C L } m\, l}{k^2} \cos. d = \text{H } m\, l \sin. d,$$

Whence we easily deduce—

$$\text{C} = \frac{\text{H } k^2}{\text{L}} \text{ tang. } d, \quad . \quad . \quad . \quad . \quad . \quad [7]$$

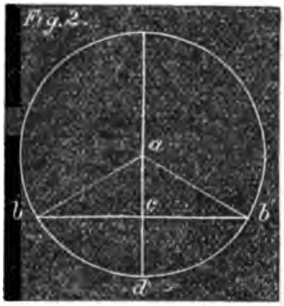
An instrument called the tangent galvanometer fulfills all the conditions referred to above. Hence with this instrument we can always determine the value of C in electro-magnetic absolute units, and thus fix the unit current. We can readily determine for any

*** The mean horizontal component for 1862 at Kew, in England, was 1·7592 units, *i. e.*, a unit pole weighing 1 gramme, and free to move in a horizontal plane would acquire under the earth's magnetism a velocity of 1·7592 metres a second.**

galvanometer at a given time and place the angle of deflection, which the unit current would produce, and then by the rule of tangents, determine the value of all other currents in terms of this unit.

Thus fixing the unit of current we find by [3] the unit of resistance, by [2] the unit of quantity, and by [1]* the unit of electromotive force.

6. The quantity of electricity in a condenser, for example a Leyden jar, may be measured by observing the swing of a galvanometer needle produced by allowing the charge to pass through the coil of a galvanometer in a time extremely short, compared with that occupied by an oscillation of the needle. The magnetic force exerted by the current may then be regarded as giving a single sudden impulse to the needle, and the strength of this impulse may be measured by the velocity, which the needle acquires on its return swing. As in the case of the pendulum this velocity is easily estimated from the amplitude of the oscillation.



In the case of the pendulum the velocity acquired in oscillating from *b* to *d* would be the same that a freely falling body would acquire in falling vertically from *c* to *d*. Calling this vertical distance *d*, we have—

$$V = \sqrt{2\, g\, d},$$

but *d* being the versed sine of the angle *b a c*, we have, when the radius is unity, and the angle *i*;

$$d = \sqrt{2\, g\, (1 - \cos.\, i)}$$

$$= \sqrt{g} \times 2 \sin.\, \tfrac{1}{2}\, i.$$

In the case of the magnetic needle the intensity of gravity is exchanged for the directive force of the earth's magnetism whose influence may be regarded for the time being, as a constant quantity. Moreover since the quantity of electricity in an instantaneous current is proportional to the velocity thus imparted we shall have—

$$Q : Q' = \sin.\, \tfrac{1}{2}\, i : \sin.\, \tfrac{1}{2}\, i'$$

* It is also true that a unit current in a straight wire, one metre long, repels another similar current in a parallel wire of the same length one metre distant, with the unit of force.

Again, calculation shows that the value of Q may be referred to the strength of the continuous current C_1, which gives the unit deflection (45°) on a tangent galvanometer by the formula—

$$Q = 2 \frac{C_1 t}{\pi} \sin. \tfrac{1}{2} i, \quad . \quad . \quad . \quad . \quad . \quad . \quad [8]$$

where t is the time of a half-oscillation.

The electro-static capacity of a conductor is the quantity of electricity with which it can be charged by the unit of electro-motive force. Hence—

$$S = \frac{Q}{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [9]$$

When the electro-motive force producing the charge, is capable of maintaining a current the capacity of the conductor may be obtained without the knowledge either of Q or E, provided we have the means of measuring the resistance of a circuit in electro-magnetic units. Let R_1 be the resistance of the circuit in which the given electro-motive force will produce the unit deflection on a tangent galvanometer then from equations [1] and [8], we have—

$$S = 2 \frac{t \sin. \tfrac{1}{2} i}{\pi R_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad [10]$$

7. *To Recapitulate.*—The electro-magnetic *unit of current* produces the unit force on a unit pole, at the unit distance, in the unit length of conductor.

The unit current conveys the *unit quantity* of electricity through the unit resistance in the unit time.

The unit current flowing through a conductor of *unit resistance*, produces an effect equivalent to the unit of work in the unit of time.

The unit current will be produced in a circuit of the unit of resistance, by the unit of *electro-motive force.*

The *unit quantity* falling in tension, the unit of *electro-motive force* does the unit of work. This last relation is, however, involved in the previous three.

8. *Names of Units.*—The units above defined are known as the *electro-magnetic absolute units*, but although exceedingly convenient as aids in calculation, they would be wholly unsuitable as practical measures of electrical quantities. These quantities are of an entirely different order of magnitudes from those which we are accustomed to measure by metrical units.

Farads.—The most powerful current ever obtained by a voltaic combination is far less than the absolute electro-magnetic unit of current, it would therefore be absurd* to adopt this unit as our ordinary measure. It has been agreed to adopt as the unit of current for ordinary purposes the 10^{-8} or $\frac{1}{100,000,000}$th part of the absolute unit. This unit we will call the B. A. unit. The quantity of electricity which such a current would discharge per second is called a *Farad* (named from Faraday). Hence the B. A. unit of current is a current of one Farad per second. The Farad is, therefore, also the 10^{-8} part of the absolute unit of quantity. We also speak of Megafarads = one million Farads, and Microfarads = the one millionth of a Farad.

Ohms.—As the absolute units of quantity are far too large for ordinary uses, so also the absolute unit of resistance is far too small. The British Association have adopted as the ordinary measure a unit called the Ohm, which equals 10^7, (ten million) absolute units. We use also Megohm = one million Ohms, and the Microhm = one-millionth of an Ohm. 48·61 metres standard copper or silver wire, 1 m.m diameter has a resistance of an Ohm at 65°.

Volts.—The British Association have adopted as the ordinary unit of tension the Volt, which equals 10^5 or 100,000 absolute units of tension, and we employ also Megavolts and Microvolts as before. A Daniel's cell has an electro-motive force of about 1 Volt. According to Thompson 1 Volt. = 0·9268 of Daniell's cell or Daniell's cell = 1·079 Volts.

The above names have been very appropriately given, since Ohm investigated the influence of resistance on electrical currents. Volta invented the battery by which electrical tension is obtained and Faraday more especially investigated the relations of electrical quantity.

9.—*Table.*

The Ohm	is 10^7	absolute units of resistance.
The Megohm	is 10^{13}	" " "
The Microhm	is 10	" " "

Ohm = 48 61 metres, copper or silver wire, 1 m.m. diameter.

The Volt	is 10^5	absolute units of electro-motive force.
The Megavolt	is 10^{11}	" " "
The Microvolt	is 10^{-1}	" " "

* The definitions on which the absolute unit of current is based, involve magnitudes never met with in practice. A unit pole cannot be realized experimentally and is therefore merely a convenient fiction.

Electro-motive force of Daniell's cell = 1·079 Volt.

The Farad is 10^{-8} absolute unit of quantity.

The Megafarad is 10^{-2} " " "

The Microfarad is 10^{-14} " " "

The units of current carry the units of quantity each second.

In using these units it must be constantly borne in mind that the letters C, E, R, Q, W, &c., given in the formulæ of the previous sections, stand in all cases for the absolute units. In calculating therefore, with B. A. units, we must substitute their values in absolute units given in the above table.

Problem.—To find the current through one Ohm with a tension of one Volt.

$$C = \frac{E}{R}; \text{ gives } C = \frac{10^5}{10^7} = 10^{-2}.$$

Ans.—One Megafarad per second.

Problem.—To find the work done by a current of one Megafarad through a resistance of an Ohm.

$$W = C_2 \, R \, t; \text{ gives } W = (10^{-2})^2 \times 10^7 = 10^3.$$

Ans.—1,000 absolute units per second.

Problem.—To find the work done by one Farad of electricity in falling in tension one Volt.

$$W = Q \, E \, ; \text{ gives } W = 10^{-8} \times 10^5 = 10^{-3}.$$

Ans.—$\frac{1}{1000}$ unit of work. Hence 1000 Volt-farads equals 1 unit of work, and 9800 Volt-farad equals 1 metre-gramme.

10. *Dimensions of Units.*—It has been shown that the units of electrical measurements may be directly referred to the fundamental units of space, weight and time—the metre, the gramme and the second; in other words, may be expressed in terms of these three quantities, and of these alone. In order to show more clearly what the relation of each is, it is proposed to give the values of the several electrical units in terms of

L = length. M = mass or weight. T = time.

$$\text{Velocity} = V = \frac{L}{T}.$$

$$\text{Force} = F = \frac{M\,V}{T} = \frac{M\,L}{T^2}.$$

$$\text{Work} = W = F\,L = \frac{M\,L^2}{T^2}.$$

$$\text{Work in metre-grammes} = \frac{M\,L^2}{T^2} \cdot \frac{1}{9{\cdot}8}.$$

$$\text{Strength of pole}^* = m = \frac{L^{\frac{3}{2}}\,M^{\frac{1}{2}}}{T}.$$

$$\text{Strength of current}^\dagger = C = \frac{L^{\frac{1}{2}}\,M^{\frac{1}{2}}}{T}.$$

$$\text{Quantity of electricity} = Q = C\,T = L^{\frac{1}{2}}\,M^{\frac{1}{2}}.$$

$$\text{Electro-motive force} = E = \frac{W}{Q} = \frac{M^{\frac{1}{2}}\,L^{\frac{3}{2}}}{T^2}.$$

$$\text{Resistance} = R = \frac{E}{C} = \frac{L}{T} = V.$$

11. *Electrical Resistance Expressed by a Velocity.*—One of the most striking results of this investigation, is that indicated by the value obtained for R, which shows that electrical resistance on the electro-magnetic system, is expressed by a velocity. The same result may be reached in another way, which will render the relation indicated more intelligible.

A current, C, in a straight conductor, of length L, crossing the lines of force of a magnetic field of the intensity S, at right angles, will experience the same force, F, as if all the points of the conductor were at the unit distance from a pole of the strength S. (See definition of unit pole and intensity of magnetic field, remembering that the action must be reciprocal between conductor and magnet). The force exerted by the conductor on a pole, S, equals, as we have seen, [5] S L C (since $k = 1$). Hence an equal force is exerted by the magnet on the conductor; or

$$F = S\,L\,C \qquad . \quad . \quad . \quad [11]$$

Let us, now, imagine a conducting wire to move perpendicular to such lines of force and to its own length. We know, by experiment, that under these circumstances, assuming that the free ends of the conductor are connected with the earth, a current is developed in the circuit. The action of the magnetic forces on this current de-

* This value is readily obtained by considering that the force exerted between two poles must be— $F = \frac{m\,m'}{D^2}$ or $= \frac{m^2}{D^2}$, when the two poles are equal. Hence— $m = D\sqrt{F}$.

† Readily derived from value of C by [5].

termines a resistance to the motion. This resistance is of course represented by [11].

If the motion is uniform, of velocity V, the work done in overcoming resistance in *the unit of time*, will, of course, be

$$W = F V = V S L C.$$

The work produces no other effect than the current, and must, therefore, be equal to the work done by the current itself in the conductor. This work by [3] is equal to $C^2 R$, and hence

$$V S L C = C^2 R, \quad \text{or}$$

$$R = \frac{V S L}{C}, \quad . \quad . \quad . \quad . \quad [12]$$

When C = S L, then R = V, that is, the value of R in electro-magnetic units is equal to the velocity with which the conductor must be moved in the magnetic field, in order that the strength of current generated shall be equal to the product of the length of the conductor into the intensity of the field; or, more simply, the resistance of a circuit is the velocity with which a conductor of unit length must move across a magnetic field of unit intensity, in order to generate a unit current.

Moreover, it can be shown that this result is independent of the magnitudes of the fundamental units to which the various values are ultimately referred, and hence that electrical resistance is measured by an absolute velocity in nature quite independently of the units of time and space in which it is expressed.

By combining [1] with [12] we easily obtain

$$E = V S L, \quad . \quad . \quad . \quad . \quad [13]$$

that is to say, the electro-motive force (or difference of tension) between two ends of a conductor moving under conditions stated, is equal to the product of the length of the conductor into the intensity of the field and the velocity of the motion, or more simply, the unit length of conductor, moving with unit velocity in a magnetic field of unit intensity (as above,) will produce a unit of electro-motive force between its two ends.

12. *Determination of the Unit of Resistance.*—It is obvious that the principles of the last section give us a second method of determining the electro-magnetic unit of resistance. The unit of resistance will be obviously a wire of such length that, when moved with unit velocity in a magnetic field of unit strength,

will generate a unit current. The experiment of moving a straight wire under the conditions assumed, would be impracticable; but, by calculation, we can pass from this simple case to the more complex one of a circular coil of known dimensions, revolving with a known velocity in a magnetic field of known intensity. Weber, from these elements, determined the absolute resistance of many wires, but this method requires the intensity of the magnetic field to be known, and the determination of this element is laborious, and its value at any one place on the earth is very inconstant. But a similar method, due to Sir W. Thompson, in which a knowledge of this element is rendered unnecessary, was employed by a committee of the British Association in determining the value of the Ohm, the B. A. unit of resistance.

In the plan of Sir W. Thompson, a small magnet screened from the effect of the air, is hung at the centre of a revolving coil. By calculation it can be shown that, when the coil revolves around a vertical axis, the couple exerted on a magnetic needle of the moment $m\ l$, when deflected to the angle d, will be

$$\text{Couple} = \frac{\text{L}^2\ \text{V}\ \text{H}}{4\ k^2\ \text{R}}\ m\ l \cos.\ d.$$

The equal and opposite couple exerted by the earth's magnetism, will be

$$\text{Couple} = \text{H}\ m\ l \sin.\ d.$$

Hence,

$$\text{R} = \frac{\text{L}^2\ \text{V}}{4\ k^2 \ \text{tang.}\ d} \qquad [14]$$

an equation from which the earth's magnetic force and the moment of the suspended magnet have been eliminated, and by which the absolute resistance can be calculated in terms of the several magnitudes of the parts of the apparatus employed.

For a description of the apparatus and mode of experimenting, see report of B. A. Committee, in the Report of British Association for 1863. The value obtained in these experiments for the coil actually used was 107,620,116 metres per second, and from this it was not difficult to construct the material Ohm of 10^7 metre-seconds.

Electro-static System.

13. *Quantity of Electricity.*—As we have no knowledge of the essence of this agent, the term quantity, as applied to electricity, conveys merely the idea of a relation between unknown magni-

tudes. In the electro-magnetic system of measurements we assume that the strength of current is proportional to its magnetic effects, and the definition of quantity immediately follows from that of current. In the electro-static system we start from a wholly different class of phenomena, and define quantity in a different way.

As is well known, two electrified bodies attract or repel each other according as they are *charged* with the same, or different kinds of electricity. Other conditions being equal, the quantity of the *charge* is assumed to be proportional to this mechanical effect; and since, if two bodies, each charged with a given quantity of electricity, are incorporated, the single body thus formed produces an effect equal to the sum of the separate effects, we are led to conclude that its charge is also equal to the sum of the separate charges. Indeed, this fact alone justifies the use of the word quantity, as applied to electricity, for we have no knowledge of the nature of the agent we call by this name.

Starting from this class of phenomena, the unit quantity of electricity would be that charge which would attract or repel an equal charge at the unit distance with the unit force. The force exerted between two electrified bodies is

$$f = \frac{q\,q^1}{d^2}, \quad . \quad . \quad . \quad . \qquad [15]$$ *

where q and q^1 represent the charges and d the distance between the electrified bodies. When q an q^1 have the same signs, f is positive and the force, as we know, is repulsion. When they have different signs, f is negative and there is an attraction.

In this connection it must be remembered—

1. That when one body is charged positively, some other body or bodies must be charged negatively to the same extent.

2. That two bodies repel one another when both are charged positively or both negatively, and attract when oppositely charged.

3. That the attractive or repulsive forces are inversely proportional to the square of the distance between the electrical charges.

4. That glass, when rubbed with silk, becomes positively electrified, while resin, rubbed with fur, receives a negative charge. Hence, a positive charge is frequently called vitreous and a negative charge resinous.

* To distinguish the electro-static units from those of the electro-magnetic system, we shall use small letters for designating the several values in the last, while we retain the corresponding capital letters for the former.

When the two coatings of a Leyden jar are connected with the poles of a voltaic battery, that united to the inactive plate receives a positive or vitreous charge, while that united to the active plate becomes charged negatively or with resinous electricity.

14. *Ratio between Electro-static and Electro-magnetic Measures of Quantity.*

The dimensions of q are $\frac{L^{\frac{3}{2}} M^{\frac{1}{2}}}{T}$.*

The dimensions of Q are $L^{\frac{1}{2}} M^{\frac{1}{2}}$.

The dimensions of $\frac{q}{Q}$ are $\frac{L}{T} = V$.

This ratio, therefore, is a velocity, and in order to pass from quantities measured on the electro-magnetic system to quantities measured on the statical system, we have only to multiply by this velocity, or

$$q = Q\ V. \qquad [16]$$

According to Weber's measurements, the velocity V = 310,740,000 metres per second, a velocity not differing from the estimated velocity of light more than the different determinations of the latter quantity differ from each other.

15. *Electrical Current.*—If two bodies, oppositely electrified like the two coatings of a Leyden jar when charged, are connected together by a metallic conductor, they lose, in a very short time, their peculiar properties, and assume a neutral condition. During the first moment of their junction the conductor is found to assume momentarily, qualities similar to those of a wire which unites the poles of a voltaic combination, and these effects are attributed to a current of electricity. The measure of this current is obviously the quantity of electricity, which passes per second, and hence in this system, as in the last,

$$c = \frac{q}{T}. \qquad [17]$$

Hence, the dimensions of the unit of current, that is the current of a unit in quantity per second, are

$$\frac{M^{\frac{1}{2}} L^{\frac{3}{2}}}{T^2}.$$

Evidently, also, $c = V\ C$.

* This value is derived from [15] for when $q = q^1$ we have $q = d\sqrt{f}$, and thence

$$L\sqrt{\frac{M\ L}{T^2}} = \frac{M^{\frac{1}{2}} L^{\frac{3}{2}}}{T}$$

16. *Electro-motive Force.*—Whenever a current passes, or in other words, electricity is transferred from one point to another, work is done. The force that does the work, and thus effects the transfer, is called the electro-motive force, and is equal to the difference of electrical tension between the two points. The work appears generally as heat or as magnetic power. This work must be, as before, [4] proportional to the quantity of electricity moved, and to the force which moves it. Just as the work done by a falling stream of water is proportional both to the quantity of water and to the height of the fall. The first corresponds to quantity of electricity, the last to the fall in tension of the electrical current. Thus we have

$$\text{W} = q\, e \text{ or } e = \frac{\text{W}}{q}. \qquad [18]$$

that is, if q units of electricity are transferred from one point to another by an electro-motive force e, the work done during the transfer will be $q\, e$, and the unit of electro-motive force is that which will do the unit work in moving the unit quantity of electricity between two given points.

We have already found that in the electro-magnetic system, $\text{W} = \text{Q}\,\text{E}$. Hence $q\, e = \text{Q}\,\text{E}$. But $q = \text{V}\,\text{Q}$, therefore

$$e = \frac{\text{E}}{\text{V}}, \qquad [19]$$

Thus to reduce electro-motive force from electro-magnetic to electrostatic measure we must divide by V. The dimensions of e are then

$$\frac{\text{L}^{\frac{1}{2}}\,\text{M}^{\frac{1}{2}}}{\text{T}}$$

17. *Resistance.*—Even when the electro-motive force between two points is constant, so that the total work done by the transfer of a given quantity of electricity remains unchanged, it is nevertheless found, that by modifying the material and size of the conductor, this transfer may be made to take place in very different times; in other words, currents of very different magnitudes are produced, and in the unit of time very different amounts of work are performed. The quality of a conductor, in virtue of which it prevents the performance of more than a certain amount of work in a given time, by a given electro-motive force, is called its electrical resistance. When, therefore, a fixed electro-motive force is maintained between its two ends, the resistance of a conductor is

inversely proportional to the amount of work done, or to the amount of electricity passed through it, in a given time. It is also inversely proportional to the current, which will be produced under these conditions. But, as we have seen, the strength of current in any conductor is directly proportional to the electro-motive force between its two ends, and both relations are most simply expressed by the formula—

$$c = \frac{e}{r},$$

which is the well known equation expressing Ohm's law. Putting this in the form $r = \frac{e}{c}$, and substituting for e and c their equivalents in electro-magnetic measure, we have—

$$r = \frac{1}{V^2} \frac{E}{C}, \text{ but since } \frac{E}{C} = R,$$

$$r = \frac{1}{V^2} R, \qquad \text{[20.]}$$

Hence to reduce resistance measured in electro-magnetic units to the electro-static equivalent, we must divide by V^2.

The dimensions of r are—

$$\frac{T}{L} = \frac{1}{V}.$$

Thus the measure of resistance on the electro-static system is the reciprocal of a velocity.

Table of Dimensions.

Quantity $q = \frac{L^{\frac{3}{2}} M^{\frac{1}{2}}}{T} = V\,Q.$

Current $c = \frac{L^{\frac{3}{2}} M^{\frac{1}{2}}}{T^2} = V\,C.$

Electro-motive force $e = \frac{L^{\frac{1}{2}} M^{\frac{1}{2}}}{T} = \frac{E}{V}.$

Resistance $r = \frac{T}{L} = \frac{R}{V^2}.$

$V = 310{,}740{,}000$ metres a second.

18. *Electro-static Capacity.*—The electro-static capacity of a conductor is equal to the quantity of electricity, with which it can be charged by the unit of electro-motive force. Let s be the capacity, q the quantity of electricity, and e the electro-motive force, then—

$$q = s\,e, \qquad \text{[21.]}$$

Hence the dimensions of s are—

$$s = \frac{q}{e} = \frac{L^{\frac{3}{2}} M^{\frac{1}{2}}}{T} \div \frac{L^{\frac{1}{2}} M^{\frac{1}{2}}}{T} = L,$$

or the electro-static capacity is represented in this system by a length only. The capacity of a condenser depends, on a great variety of conditions, but calculation shows that the capacity of a spherical conductor in open space is equal to the radius of the sphere.

The relation of the electro-static to the electro-magnetic unit of capacity is expressed by the equation—

$$s = v^2 S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [22.]$$

19. *Specific Resistance.*—On account of the difficulty of measuring with accuracy the diameters of wires it is more convenient to refer the resistance to the mass or weight in a given length than to the section.* The specific resistance of a material is the resistance of the unit weight made into a conductor of the unit length. Thus the specific resistance of copper is the resistance of a wire of that metal weighing one gramme and one meter long. If the same weight of metal be drawn out into a wire of twice the length it is obvious that the section of the wire will be diminished in the same proportion. Hence the resistance will be doubled on account of the increased length, and doubled again on account of the diminished section. So in any case *the resistance of the same weight of metal varies as the square of the length of the conductor, which it forms.* Assuming now the weight to be constant, it is evident (since the section of the same length of wire must be proportional to its weight) that *the resistance of a given length of conductor is directly proportional to its weight.* Thus we deduce for the value of the resistance of any conductor in terms of its weight and length the expression—

$$R = \frac{(\text{Sp. R.}) \times l^2}{w}, \quad . \quad . \quad . \quad . \quad . \quad [23.]$$

The specific resistance of pure copper at 60° C. is 0·1523 Ohm, but it changes very rapidly with the temperature.

20. *Specific Inductive Capacity.*—Faraday discovered that the capacity of a conductor does not depend solely upon its dimensions or on its relations to other conductors, but is greatly influenced by the nature of the insulator or dielectric, separating it from them. The name inductive-capacity is given to that quality of an insulator,

* As is well known, the resistance of any homogeneous wire, of uniform size, is directly proportional to the length, and inversely proportional to the area of the section, or the square of the diameter.

in virtue of which it affects the capacity of the conductor it surrounds, and this quality is measured by reference to air, which is assumed to possess the unit inductive capacity. The specific inductive capacity is therefore the ratio of the capacity of any conductor insulated by that material, to the capacity of the same conductor, in the same position separated from surrounding bodies by air alone.

Calculation of Derived Currents.

21. *Shunts.*—When an electrical current branches into two or more streams, it is said to be shunted, and any conductor which diverts a portion of the current from the main circuit is called a *shunt*, contracted from shun it.* The several subordinate streams thus formed are called *derived currents*, and it becomes of great importance in telegraphy to be able to calculate the quantity of electricity flowing in each. Moreover, several of the most valuable methods of electrical measurement are applications of the theory on which these calculations are based.

Since the several derived circuits, into which the main stream divides, may branch off at the same or at different points, and may either return on the same conductor or may flow to the earth ("make earth") through separate channels; moreover, since the original electro-motive power may be reinforced at any point, it is obvious that cases of great complexity may arise under the general theory. All such problems, however, may be solved by the application of two simple principles, the definite statement of which we owe to Kirchhoff.

22. *Kirchhoff's Laws.*—The following propositions are deductions from the general theory of electrical currents, and have been proved both mathematically and experimentally.

1. *The sum of the currents which approach any point is always equal to those which recede from it.*

Or if we distinguish the first by a plus, and the second by a negative sign we may say more generally;

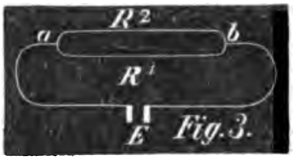
The sum of all the currents which meet at a point is equal to zero.

2. *On any continuous line of conductors, the sum of the products of the resistances of the several parts by the strength of the current in each part, is equal to the sum of the electro-motive forces included in the same closed circuit.*

* A galvanometer, for example, is said to be shunted when only a portion of the current to be measured passes through it, the rest flowing through a wire (*the shunt*), which connects the two binding cups of the instrument.

This last proposition holds true of every circuit which may be traced in any system of conductors and batteries, however complicated the maze; only currents flowing in opposite directions with reference to the given circuit, must be distinguished by opposite signs. Moreover, the sum is equal to zero when there is no electro-motive force on the line of conductors under consideration.

23. *Application to a Simple Shunt.*—In Fig. 3 let E represent the electro-motive force of the voltaic element which determines a current of strength C; let R represent the total resistance in the main conductor *a* E *b* through which the whole current flows: let R_1 and R_2 represent the resistances of the two conductors *a* R_1 *b* and *a* R_2 *b* through which flow the two derived currents C_1 and C_2, respectively. We have then by the first of Kirchhoff's laws whether we consider the points *a* or *b*.



$$C = C_1 + C_2 \text{ or } C - C_1 - C_2 = 0, \quad . \quad . \qquad [24.]$$

The second law now gives us—

$$C\,R + C_1\,R_1 = E, \quad . \quad . \quad . \quad . \qquad [25.]$$

$$C\,R + C_2\,R_2 = E, \quad . \quad . \quad . \quad . \qquad [26.]$$

$$C_1\,R_1 - C_2\,R_2 = 0, \quad . \quad . \quad . \quad . \qquad [27.]$$

From [25] and [26] we at once deduce—

$$C_1 = \frac{E - C\,R}{R_1}, \text{ and } C_2 = \frac{E - C\,R}{R_2}.$$

Then substituting these values of C_1 and C_2 in [24], we obtain further—

$$C - \frac{E - C\,R}{R_1} - \frac{E - C\,R}{R_2} = 0,$$

and lastly by reduction we find that—

$$C = E\,\frac{R_1 + R_2}{R\,R_1 + R\,R_2 + R_1\,R_2}, \quad . \quad . \quad . \qquad [28.]$$

We can now, by substituting this value of C in [25] and [26], obtain the corresponding values of C_1 and C_2 as follows:—

$$C_1 = E\,\frac{R_2}{R\,R_1 + R\,R_2 + R_1\,R_2} \quad . \quad . \quad . \qquad [29.]$$

$$C_2 = E\,\frac{R_1}{R\,R_1 + R\,R_2 + R_1\,R_2}, \quad . \quad . \quad . \qquad [30.]$$

The well known effects of shunts are direct inferences from these equations. Thus from [29] and [30] we obtain—

$$C_1 : C_2 = R_2 : R_1, \quad . \quad . \quad . \quad . \quad . \quad . \qquad [31]$$

That is the strengths of the currents in the two branches are inversely proportional to the resistances in the two channels into which the main stream divides.

By comparing [28] with [29] or [30] we have—

$$C_1 : C = R_2 : R_1 + R_2 \text{ and } C_2 : C = R_1 : R_1 + R_2.$$

$$C_1 = C \frac{R_2}{R_1 + R_2}. \quad C_2 = C \frac{R_1}{R_1 + R_2}, \quad . \quad . \qquad [32.]$$

Hence the fraction of the stream, which passes through a derived circuit, or, in other words, the reducing power of a shunt is found by dividing the resistance of the shunt by the resistance of the shunt plus that of the derived circuit. If, for example, in Fig. 3, R_2 is the resistance of a galvanometer equal to 99 Ohms and R_1 the resistance of a shunt equal to 1 Ohm, then only $\frac{1}{100}$ of the primary current will pass through the galvanometer, and the shunt reduces its effect on the instrument to that extent.

Finally, we can readily find the *equivalent resistance* of such a branched circuit; for we know by Ohm's law that the total resistance of the whole circuit, including the battery, is—

$$R_0 = \frac{E}{C},$$

and from this we obtain, by substituting the value of C from [28.].

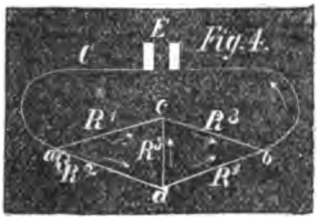
$$R_0 = R + \frac{R_1 R_2}{R_1 + R_2} = R + \frac{1}{\frac{1}{R_2} + \frac{1}{R_1}}, \quad . \qquad [33.]$$

The last term in the above expression evidently represents the equivalent resistance of the two branches R_1 and R_2. If there were three branches instead of two the value would be—

$$R_0 = R + \frac{1}{\frac{1}{R_3} + \frac{1}{R_2} + \frac{1}{R_1}}, \quad . \quad . \quad . \qquad [34.]$$

and hence in general the *equivalent* or joint resistance of any number of branches may be found by adding together the reciprocals of the resistances of each branch and taking the reciprocal of this sum.

24. *Wheatstone's Bridge.*—We have represented in Fig. 4 a system of derived currents, devised by Sir Charles Wheatstone, which is very much used for comparing the resistances of different wires. The battery current C divides at *a* into two branches *a c b* and *a d b*. Two intermediate points *c* and *d*, on these branches are connected by a conductor, which includes a galvanometer. This conductor is called the bridge, and it can be shown that no current will flow over the bridge when the resistances of the several parts of the circuit are such that—



$$R_1 : R_2 = R_3 : R_4, \quad . \quad . \quad . \quad . \quad . \quad [35.]$$

Furthermore, as the galvanometer indicates the smallest current, we can tell when, on varying the resistances, we have reached the condition of equilibrium, and we have then the means of calculating the fourth resistance, assuming that the other three are known. In practices R_1 and R_2 are usually resistance coils of definite values, while R_3 is a set of coils, whose resistance[1] may be varied at pleasure and R_4 is the conductor whose resistance is to be measured.

The proportion on which this very accurate method of measurement depends may be easily deduced by a simple application of the laws of Kirchhoff. From the first law we have for the currents meeting at *c* and *d*.

$$C_1 - C_3 + C_5 = 0. \text{ and } C_2 - C_4 - C_5 = 0, \quad [36.]$$

From the second law we have for the circuit *a*, *d*, *c*.

$$C_1 R_1 - C_5 R_5 - C_2 R_2 = 0, \quad . \quad . \quad . \quad [37.]$$

and for the circuit *a*, *c*, *b*, *d*.

$$C_1 R_1 + C_3 R_3 - C_4 R_4 - C_2 R_2 = 0, \quad . \quad [38.]$$

When there is no current between *d* and *c*, $C_5 = 0$. Hence in the condition of equilibrium we have by [36]—

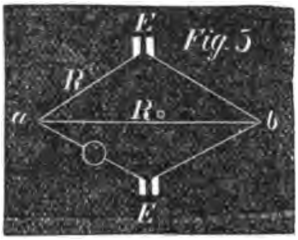
$$C_1 = C_3 \text{ and } C_2 = C_4.$$

Moreover, by [37] $C_2 = C_1 \dfrac{R_1}{R_2}$.

Substituting now these values in [38], we obtain an equation between the several resistances alone, from which we at once deduce—

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}, \text{ or } R_1 : R_2 = R_3 : R_4.$$

25. *Poggendorff's Method* of measuring the electro-motive force of a voltaic element by comparing it with some standard cell is another beautiful application of the theory of derived currents. Two voltaic elements, E and E^1, Fig. 5, ($E > E^1$,) are united by the poles of the same name. Between the points *a* and *b* on the connecting wires, we insert a set of resistance coils R_0. We thus establish two associated lines of conductors, first, E, *a*, *b* having a total resistance of $R + R_0$, and secondly, E^1, *a*, *b*, whose resistance it is not nececessary to consider. In the second circuit is included a galvanometer. When E is greater than E^1 it is possible by varying the resistance R_0, so to neutralize the effect of the weaker element that no current shall pass through the second circuit as will be indicated by the galvanometer. When this is the case we have by Kirchhoff's second law for the two circuits—



$$(1.)\ C\,(R + R_0) = E. \quad (2.)\ C\,R_0 = E^1.$$

Hence—

$$\frac{E^1}{E} = \frac{R_0}{R + R_0}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad [39.]$$

an equation which enables us to measure E^1 in terms of E, or the reverse, whenever the values R and R_0 are known. The value of R_0 is given by our coils, but since the resistance R is chiefly that of the element E it is difficult to measure it with accuracy. We may avoid the necessity of determining this uncertain element by adding to the part of the circuit E, *a*, the further resistance R^1. It will then be necessary to increase the resistance of the coils between *a* and *b*, to bring the galvanometer to rest. Call this quantity R_1. We shall now have a second equation—

$$\frac{E^1}{E} = \frac{R_0 + R_1}{R + R^1 + R_0 + R_1},$$

and by comparing this with the last, we deduce—

$$\frac{R_1}{R^1 + R_1} = \frac{R_0}{R + R_0}$$

Hence—

$$\frac{E^1}{E} = \frac{R_1}{R^1 + R_1}, \quad . \quad . \quad . \qquad [40.]$$

HEAT OF FRICTION.

[From the Proceedings of the American Academy of Arts and Sciences, Vol. VI., April, 1865.]

ON THE HEAT OF FRICTION.

BY

Prof. JOSIAH P. COOKE, Jr.

An accident to one of the large turbine wheels employed by the Merrimack Manufacturing Corporation of Lowell has furnished a most remarkable illustration of the modern mechanical theory of heat, and through the kindness of Mr. Isaac Hinckley, the accomplished agent of the Corporation, I have the pleasure of bringing the facts to the notice of the Academy. I cannot do better than to begin by reading Mr. Hinckley's own statement, in a letter addressed to me, dated December 30th, 1864. The specimens referred to in the letter I have placed on the table for the inspection of the Academy.

"In accordance with your request, I herewith send you five pieces of metal, once portions of one of our turbines. I have placed these pieces in the box in the same relative positions which they occupied when they made a part of the turbine. To make my statement clear to you, I would refer to Plate I. of Mr. Francis's admirable work, 'Lowell Hydraulic Experiments,' which you will find in the College Library. Our turbines are similar to the Tremont turbine therein shown.

"The turbine of which these pieces were a part is one of 250 H. P., under a fall of 32 feet, using 75 cub. ft. of water per second. The wheel is of 58½ inches diameter, with depth of float of 6 inches, and a velocity

of 144 revolutions per minute. Its position is horizontal, and at a level of 3 feet below the surface of Merrimack River at its ordinary stage. It is mounted upon a vertical wrought-iron shaft 25 feet long and 6 inches diameter at smallest place. This shaft is fitted at its upper end with a series of disks, by means of which it is supported in its box, which again is supported by a massive cast-iron frame. This frame supports the entire weight of the wheel and shaft. The shaft at its lower end is bored in the line of its axis to a depth of 5½ inches to receive a steel pin of 17½ inches length and 2½ inches diameter; and which projects from the shaft 12 inches. The steady-pin has no function to perform other than that of restraining the shaft from lateral aberration. It is free to revolve in a box made of three pieces of case-hardened iron, so placed in a cast-iron frame as to allow free play to the steady-pin and the free access of water to it. Each of these three pieces composing this box is kept up to its place by following-screws working in the cast-iron frame which is bolted to the stone floor of the turbine pit. In the Tremont turbine this floor is of wood, and in Plate I. the steady-pin is marked 'I.'

"The pieces sent are marked Nos. 1 to 5. No. 1 is the portion of the steady-pin which was nearest the shaft; No. 2, the other extremity of the same pin; Nos. 3, 4, 5, the three pieces of case-hardened iron forming the box, with portions of the steady-pin attached. You will at once perceive that this steel has been partially fused, and can thus account for its attachment to the iron.

"The facts are, that on noticing some irregularities of motion on the part of the wheel, it was stopped, and the water pumped from the pit until the floor was bare. Inspection showed that the following-screws had not done their duty uniformly; and the three pieces, Nos. 3, 4, 5, no longer preserved their proper relative positions, nor allowed free play to the steady-pin. The consequence was, an amount of friction causing heat sufficient to fuse steel, although the latter was immersed three feet deep in a raceway ten feet wide, through which was passing seventy-five cubic feet of water per second.

"A similar accident happened thrice to our turbines, which are now, however, safely guarded against such mishaps."

There are two points in connection with these facts to which I wish especially to call attention. In the first place, the weight of the wheel did not rest upon the surfaces of friction. The three pieces of case-hardened iron in their displaced position acted simply as a brake

upon the revolving shaft, so that the heat must have resulted wholly from the destruction of mechanical motion. The immense moving power of the wheel, instead of being directed wholly into its appropriate channel, was in part transformed into that mode of atomic motion called heat. In the second place, the temperature attained was at least the welding-point of iron, and this, too, although the heated metal was immersed in a stream of flowing water. It is undoubtedly true, that the spheroidal condition of the water would greatly retard the loss of heat, but still the loss must have been exceedingly rapid. Now the loss, even at the highest temperature attained, must have been fully supplied by the heat generated during the same time; and this must, therefore, have been evolved with equal rapidity at the surfaces of friction. No change in the molecular condition of the iron, and no abrasion of the metal, is at all sufficient to account for this continuous, prolonged, and immensely rapid evolution of heat, and the facts force upon us the conclusion, that the destruction of mechanical motion is the one and only efficient cause. Moreover, if we admit the generally received principle of mechanics, that motion cannot be annihilated, the conclusion that heat is a mode of motion is equally irresistible. Lastly, it is evident that the facts here stated perfectly accord with the well-known experiments of Rumford and Davy; only since the moving power of the Merrimack turbine is so much greater than that employed by these distinguished experimentalists, the results which I have had the pleasure of exhibiting are more striking and conclusive than any which have been previously obtained.

PROJECTION OF THE SPECTRA OF THE METALS.

[From the American Journ. of Science and Arts, Vol. XL, Sept., 1865.]

ON THE PROJECTION

OF THE

SPECTRA OF THE METALS.

By Prof. JOSIAH P. COOKE, Jr.

Spectrum analysis has become, in all its bearings, a subject of so much importance both in chemistry and physics, that a simple and efficient method of exhibiting the phenomena to an audience is an important need to all teachers of physical science. Having tried several plans without obtaining the definiteness or brilliancy required, I finally devised the following, which has been completely successful. By placing my lantern at the distance of from 50 to 60 feet from the curtain, I obtain a spectrum from 20 to 25 feet in length and about 18 inches in breadth, with all the brilliancy that can be desired and without any diffused light, which greatly impairs the beauty and distinctness of the phenomena as they have been hitherto exhibited. My apparatus may be best described under three heads: First, the electric regulator; secondly, the lantern with the adjustable slit and lenses; and, lastly, the prisms for dispersing the light.

The light is obtained by means of a powerful galvanic battery. I have found that fifty Bunsen cells of medium size (about 7 inches high) were quite sufficient. The metal whose spectrum is required, is volatilized in the voltaic arc and almost

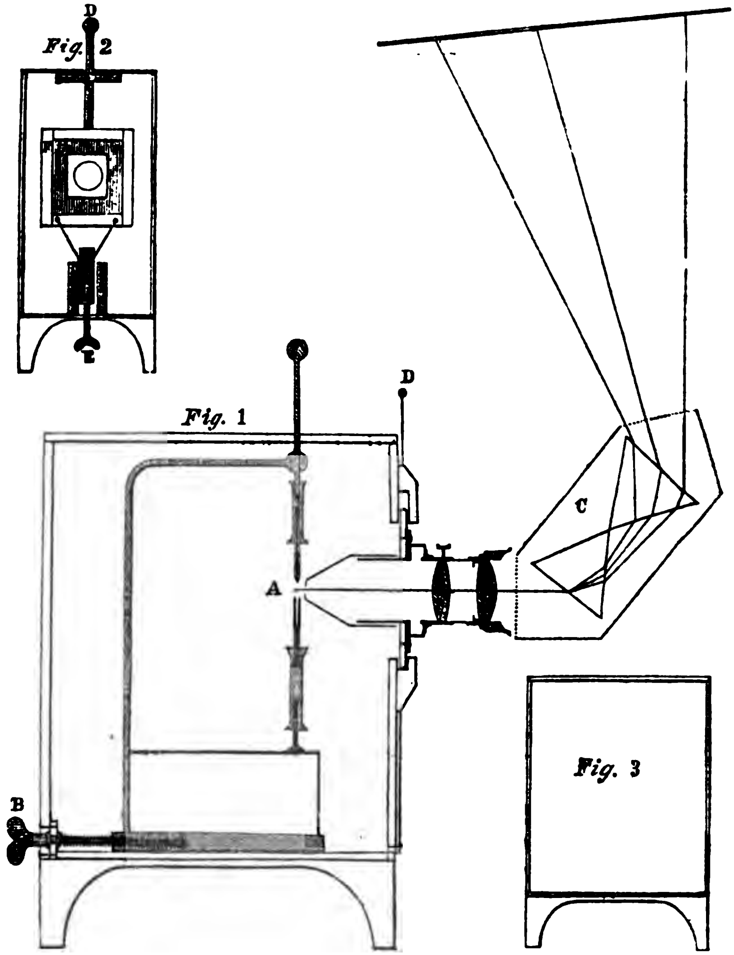


Fig. 2

Fig. 1

Fig. 3

any of the numerous electric regulators may be used for the experiment. I used for a long time a Deleuil regulator, and in fig. 1 a section is shown of this regulator in connection with the rest of the apparatus. I now use, however, a regulator better adapted to the purpose, made by J. Duboscq, of Paris. The negative pole, which is the lowest, is formed of a small cylinder of hard coke, having a small cavity at the top to receive the

metal. The positive pole is formed of a coke pencil such as is used in most electric lamps. The poles are so arranged that they can be raised or lowered at will, and the milled heads, which regulate the motion, are placed for convenience at the base of the instrument. The coke cylinder forming the negative pole is fastened to the rim of a circular brass disk, which also supports four other similar cylinders. So that, by turning the disk, one after the other may be brought under the positive pole, and different metals volatilized in the voltaic arc without further adjustment.

The electric regulator is placed within a dark lantern, as shown in fig. 1, resting on a movable platform, which can be moved backward or forward by the screw B. The lantern is made of wood like a square box, see figs. 1, 2 and 3, with doors on two opposite sides as large as the box will permit. The upper part of each door is made of wood and hung on hinges in the usual way; but from this is suspended a thick cloth curtain, which, while covering the lower part of the doorway, enables the experimenter to adjust the poles without opening the lantern. The wooden doors, moreover, are glazed with very deeply colored glass in double plates of blue over red through which the experimenter can see the carbon poles when ignited by the galvanic current.

The electric regulator is placed in the lantern so that the carbon poles shall be directly behind and within half an inch of an adjustable slit, which should be about half an inch high and $\frac{1}{16}$th to $\frac{1}{8}$th of an inch wide. This slit forms a part of a brass cap which slides on one end of a brass tube, while into the other end is screwed a camera tube such as is used by photographers for taking portraits. The lenses of the combination which I use are three inches in diameter, and the focal length is about $5\frac{1}{2}$ inches. This size cannot be advantageously exceeded, but the shorter the focal length of the combination the better. The slit is placed at the focus of the combination, and the position of the lenses with reference to the slit is adjusted by means of the rack and pinion usually attached to camera tubes. The brass tube with the slit and lenses just described is fastened to a thin board, which slips into a movable wooden frame on the front of the lantern, (see fig. 2), a portion of the tube with the slit projecting into the box, as shown in fig. 1. The object of the movable frame is to adjust rapidly the position of the slit with reference to the voltaic arc, so as to keep the slit constantly in front of the luminous flame, which, as is well known, shifts its position from one side to the other of the carbon poles in a most irregular manner. The means of adjustment just referred to are shown in fig. 2.

The frame F is connected by iron bars with a pivot which turns in the wooden block G. Moreover, to the top of the frame there is attached a flat iron bar, which ends in the handle D, a stout steel spring attached to the front of the box serving to keep the bar in place although permitting a slight lateral motion. By moving then the handle D the slit with the lenses may be moved to one side or the other, as the position of the flame may require. Finally, the bar G slides between two grooved wooden bars, and may be moved by the screw E. Thus the frame may be raised or lowered, and the slit kept constantly midway between the carbon poles.

It remains now to describe the prisms, by which the light is dispersed. I use for the purpose two large sulphid of carbon prisms having a refractory angle of 60°. They were made from a large and thick glass tube three inches in diameter, with faces of ordinary plate glass cemented to the cells with a mixture of glue and molasses. They are securely fastened in a wooden box, which is made of such a shape that when the light passes at the angle of least deviation the rays will enter the box perpendicular to one side, and will leave it perpendicular to another. The box is closed except at the two ends, in which circular apertures are made three inches in diameter, and these can be closed with covers when the prisms are not in use. A section of the box and prisms is shown at C, fig. 1. It is here drawn on the same plane as the section of the lantern, but when in use it is at right angles to this plane.

Having a knowledge of the various parts of the apparatus, the method of using it can be readily understood. The lantern having been placed on an elevating stand with a revolving table[1] at a distance of 50 or 60 feet from a curtain or white wall, the prism box is placed at one side on a similar table, and adjusted so that, while the axis of one of the circular openings is perpendicular, or nearly so, to the screen, the axis of the other opening will coincide with the axis of the lenses when the lantern is turned on the revolving table through the required angle; see fig. 1. The lantern being now directed to the screen, the electric regulator having been adjusted so that the point of contact of the carbon poles is in the axis of the lenses and about two inches behind the slit, and the galvanic circuit having been closed so as to produce the electric light, the focal distance of the lenses is so adjusted as to form a distinct image of the slit on the screen. We then turn the lantern on the revolving table so that the light shall pass through the prism, and we have at once the projection of the spectrum in all its beauty over 20 feet in length and 18 inches or more in breadth. To

[1] The stands used by photographers are well adapted for the purpose.

produce now the spectrum of a metal we first separate the poles, and then bring them, by the aid of the screw B, within half an inch of the slit. Having now placed a small piece of the metal selected for the experiment in the cavity of the coke-cylinder, we again bring the poles in contact and slowly separate them as the heat increases, until the light emitted by the ignited carbon is wholly intercepted by the edges of the slit and the lenses are illuminated only by the ignited vapor between the poles. We then have the spectrum of the metal, which continues in perfect purity so long as the space between the poles remains filled with the metallic vapor. When, however, the supply diminishes, either in consequence of the consumption of the metal, or on account of the failing strength of the battery, the bright bands, which distinguish the elements of the air, will appear at the same time with those of the metal. The metals which I have found best adapted to these experiments, are copper, zinc, brass (which gives the bands of copper and zinc together), mercury, thalium, sodium, lithium, potassium, cadmium, antimony, lead, gold and silver; and of these the first seven give the most characteristic and brilliant results. I use them all in the metallic state with the exception of lithium, which I use as carbonate, moistening the salt before placing it on the pole. It is important to have a separate coke cylinder for each metal, as otherwise, unless the cavity is most carefully cleaned out between the experiments—and for this there generally is no time—the spectra will be confused by the reappearance of the bands of the metals previously used.

These experiments can be varied by projecting on the screen the image of the carbon poles with the stream of glowing vapor between them, and thus showing the color of the light before it is decomposed; and for this purpose it is only necessary to direct the lenses to the screen, and, having removed the brass cap, which carries the slit, to re-adjust the focal distance of the lenses.

The reversal of the sodium band can also be readily shown. For this purpose we arrange the apparatus so as to produce a continuous spectrum, as first described. We then interpose between the poles and the slit the flame of a Bunsen lamp, and in this flame we insert a small spoon containing metallic sodium. A dark line soon appears crossing the yellow portion of the spectrum in the position of the sodium band. It is convenient to have a small shelf in the box, to support the lamp, so hung on hinges that it will drop out of the way when its support is removed.

Again, the formation of dark lines crossing the spectrum, similar in appearance to the solar lines, can be shown by interposing between the lenses and the prism a vessel with parallel

glass sides containing hyponitric acid or iodine vapor. Such a vessel is easily made from a piece of glass tubing—three inches in diameter and four inches long—by cementing plates of glass to the open ends and drilling a hole through the sides, into which a glass stopper may be fitted.

Finally the apparatus may be with a little additional expense so constructed that it can also be used for projecting photographic transparencies after the principle of the magic lantern. Small photographs on glass may thus be used in place of diagrams and the great geological features of our globe, the glaciers for example, may in this way be brought before the eyes of an audience with almost all the vividness of the reality. The same method of illustration will be found of great value in teaching other sciences. For instance, the best way of giving an idea of the dark lines of the solar spectrum is to take a photograph of the more refrangible portion and project the image on the wall. Such photographic transparencies are easily made; but as few teachers have the means or time for such work, it would be well if some professional photographer would turn his attention to this department of his art. If the instrument here described is to be used as a magic lantern it is necessary to have, besides the regulator above described, a second adapted for giving continuous light. We have used for some time the regulator now made by J. Duboscq of Paris, after the plan of Foucault, and we find that it works very well.

Most of the apparatus here described is so simple that it can be made by any good mechanic and for this reason we have entered into more detail than would otherwise be necessary. The lenses and other accessories must of course be purchased. The apparatus can also be ordered from E. S. Ritchie & Co. of Boston.

Cambridge, August 8th, 1865.

[From the American Journ. of Science and Arts, Vol. XL, Nov., 1865.]

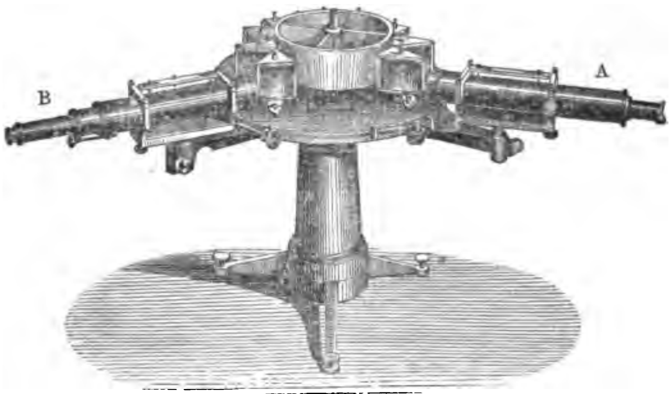
On the Construction of a Spectroscope with a number of prisms, by which the angle of minimum deviation for any ray may be accurately measured and its position in the solar spectrum determined.

BY JOSIAH P. COOKE, Jr.

In an extract from a letter of the author published in this Journal, vol. xxxvi, p. 266, a method of adjusting the prisms of a compound spectroscope was described, by which the adjustment for any portion of the spectrum could be obtained with great rapidity and accuracy. A further study of the subject has shown that the method of adjustment then only briefly described admits of the highest precision, and may be applied to the exact measurement of the angle of minimum deviation of the spectrum rays. It has been thus possible to apply the great dispersive power of the large Cambridge spectroscope in determining the relative position of the various spectrum lines, and to secure all the accuracy of which angular measurements are capable. The value of such measurements is obvious, and with the hope that this method will prove to be an assistance to investigators we propose to give in this paper a description of our instrument and of the manner of using it.

The general construction of the instrument is shown in fig. 1.

1.

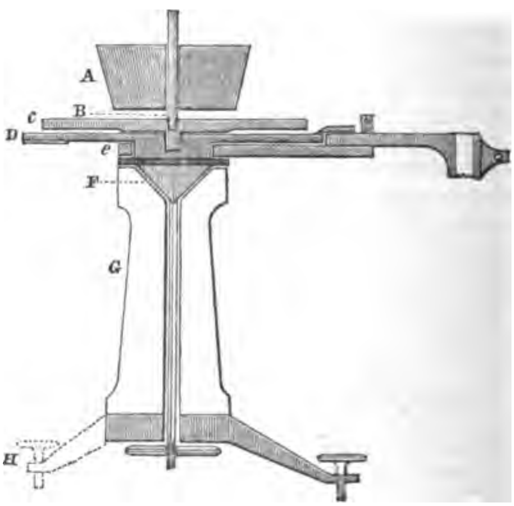


The two telescopes are constructed in the usual way. The telescope A, which we shall call the collimator, has an adjustable slit placed exactly at the focus of the object glass. The small tube which carries the slit slides into the body of the telescope, but a rack and pinion motion would be preferable, so that when the focus is changed the slit will necessarily remain vertical. The rays of light diverging from the slit and rendered

parallel by the object glass of the collimator next pass through a series of prisms adjusted around a conical wheel, which will be soon described, and are then received by the telescope B. The spectrum, which is formed at the focus of the object glass of this telescope, is examined with eye-pieces of different magnifying powers in the usual way. The object glasses of the telescopes are 2½ inches in diameter and have a focal length of 15½ inches. They rest in Y's and are provided with spirit levels and adjusting screws. The frames which hold the telescopes are supported on pivots turning in sockets at the ends of two arms connected with the body of the instrument and may be clamped in any position. The arm which carries the collimator is permanently attached to the main iron plate, but the arm, which carries the observing telescope may be moved around the plate.

The details of the construction are shown in fig. 2, which is a section made through one of the legs of the tripod and the movable arm, the telescope with its frame and pivot having first been removed from the socket. (This figure as well as fig. 4 were drawn to the scale of one inch to a foot). The parts are as follows: H is an iron tripod with leveling screws; G is a hollow mahogany column with a conical cavity at the top; F is an iron cone which rests in the conical cavity, supporting the whole body of the instrument and connected by a long iron rod with a clamping screw beneath the tripod. By means of this arrangement the instrument may be turned as a whole in the horizontal plane and the collimator directed to the source of light. Above the iron cone and fastened to it securely is the main circular plate of the instrument, which is 18 inches in diameter and ½ an inch in thickness. Near the outer edge of this plate is inserted a band of silver, which is graduated to 10″ of arc. On the under part of the plate there is a neck and at the center of the upper surface a socket, which are accurately centered with each other and with the graduated limb. Around the neck at E moves an iron collar, to which is attached

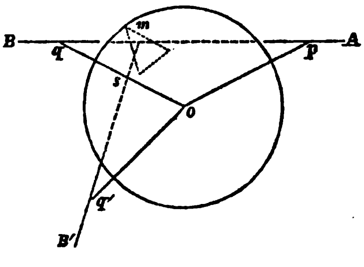
2.



the arm bearing the observing telescope. This moves, therefore, concentric with the graduated limb and bears a vernier by which the angular motion may be determined, reading to 10″. In the socket of the first plate rests the pivot of a second plate, C, which turns on the first and supports the prisms with the adjusting wheel A. The diameter of the upper plate is an inch less than that of the lower plate, so as to expose the graduated arc near the outer edge of the latter, and its upper surface is as flat and even as possible. Rising from the center of the upper plate there is a tall screw pivot of iron, B, on which turns a conical wheel, made also of iron. By this motion the wheel may be either raised or lowered. This wheel is an essential portion of the instrument, and we will next consider the theory of its use.

In the ordinary method of measuring the angle of minimum deviation with a Babinet's goniometer the prism is placed on a revolving plate at the center of the graduated circle, and so adjusted that the edge of the refracting angle shall be perpendicular to the plane of the circle, and its bisectrix parallel with a diameter of the circle. The axis of the collimator and observing telescopes, moreover, being parallel with a diameter of the circle, it is evident that, when the prism and telescope are turned into the position of minimum deviation, the vertex of the angle of minimum deviation will coincide with the center of the circle, and hence the arc intercepted between two radii of the circle parallel to the axes of the two telescopes will be the measure of the angle required. This angle is practically measured by first bringing into line of collimation the observing telescope and collimator, so that the image of the slit at the end of the collimator coincides with the vertical wire in the eye-piece of the telescope. The position of the vernier on the graduated arc is now noted. Then, having adjusted the prism, both the prism and the telescope are turned to the position of minimum deviation, and a coincidence established between the vertical wire and one of the lines of the spectrum. The vernier is now again read and the difference between the two readings is the angle of minimum deviation for the ray corresponding to that line.

3.



It will be obvious however from fig. 3, that it is not necessary for the accuracy of this measure either that the prism should be placed at the center of the circle, or that the axes of the telescope should be parallel to one of its radii. If only the bisectrix of the refracting angle passes through the center of the circle, the prism

may be placed on the outer rim of the plate, and if only the radial arm, which carries the observing telescope, moves concentric with the graduated arc, the axis of the telescopes themselves may make any angle with the radius whatever. Let O*p* and O*q* be two radii of the graduated circle. Let A*p* and B*q* represent the axes of the two telescopes in collimation and making any undetermined angles with the two radii. Place now a prism at *m* and turn the radial arm O*q* into the position O*q*′, but without changing the inclination of the axis of the telescope to the arm, and let B*m*B′ be the angle of minimum deviation. Since now the two triangles *qsm* and *q′so* are similar, it is evident that the angle B*m*B′ is equal to the angle *qoq′*, and is therefore measured by the arc intercepted between the radii O*q* and O*q′*.

In order now to apply this principle in the spectroscope the glass prisms were mounted permanently in brass frames. The frames rest on three brass pins which were adjusted by filing until the refracting edge of the prism was perpendicular to the iron place C fig. 2. Two brass pins were also attached to the back of each prism and the lengths of these so adjusted that, when the prisms are pushed against the conical wheel, the bisectrix of the refracting angle should coincide with a radius of the wheel. The last adjustment was made with the aid of a guage cut from a sheet of tinned iron fitting at the same time the periphery of the wheel and the face of the prism, which was applied alternately on either side. The angle of minimum deviation of the ray D was then measured for each prism in the following way:—

The prism having been placed on the plate with the pins applied to the periphery of the wheel, the collimator was turned on its pivot, and at the same time the plate C turned on its center, until on applying the eye at the open slit and looking through the object-glass towards the prism, the further back edge of the prism, seen through the glass of the prism, appeared to coincide with the nearer back edge seen directly. When this is the case it is evident that the rays of light which reach the eye from the further back edge of the prism must pass through the glass parallel to the back edge of the prism, or, what amounts to the same thing, perpendicular to the bisectrix of the refracting angle, and when the light passes in this way the prism is at the angle of minimum deviation. When the prism was thus placed the collimator was turned slightly on its pivot until the axis of the telescope prolonged passed through the center of the prism-face, and was then securely clamped in this position. This adjustment may be made with sufficient accuracy by the unassisted eye. The prism having now been turned one side, the arm of the observing telescope was turned on its center, and at the same time the telescope turned on its pivot until it came into exact collimation with

the collimator. In order to facilitate this adjustment the telescopes are provided with caps which cover the object-glasses of the telescopes with the exception of a narrow vertical slit at the center. The pivot of the observing telescope was next clamped and the caps having been removed the image of the slit seen through the observing telescope was brought into exact coincidence with the vertical wire and the position of the vernier noted. The prism was now brought back to its place by turning the upper plate of the instrument, and the observing telescope also turned until the position of minimum deviation for the ray D was attained and this well known double line brought to coincide with the vertical wire. The limb was then again read, and the difference of the two readings gave the angle of minimum deviation for the prism.

In order to show that this method of measurement is perfectly accurate, we give below the angles of minimum deviation of the nine prisms of the Cambridge spectroscope measured as just described, and in a parallel column the same angles measured in the old way with the prisms at the center of the plate. It will be seen that the differences are insignificant and within the limits of error of observation:

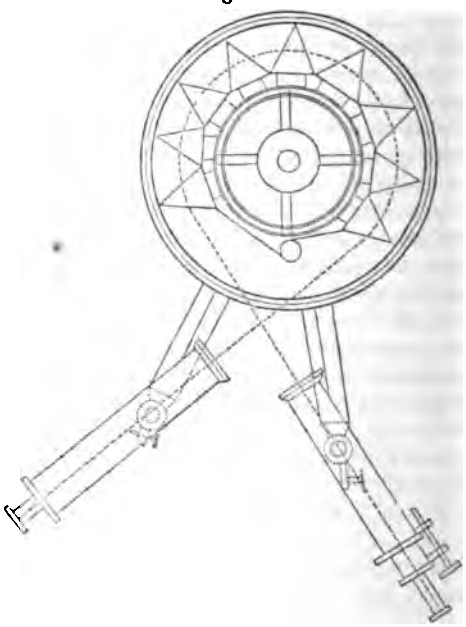
	Measured at center of plate.	Measured on edge of plate.	
No. 1,	29° 31′ 10″	29° 31′ 10″	
No. 2,	29° 29′ 10″	29° 29′ 10″	
No. 3,	29° 28′ 10″	29° 28′ 10″	
No. 4,	29° 37′ 0″	29° 36′ 40″	−20″
No. 5,	29° 28′ 30″	29° 28′ 40″	+10″
No. 6,	29° 36′ 30″	29° 36′ 10″	−20″
No. 7,	29° 28′ 10″	29° 28′ 10″	
No. 8,	29° 29′ 30″	29° 29′ 40″	+10″
No. 9,	29° 28′ 40″	29° 29′ 40″	
	267° 37′ 50″	267° 37′ 30″	−20″

Although the adjustments required may appear complicated, they can be made in far less time than it has taken to describe the method.

It is a well known fact that when a beam of homogeneous light passes through a prism at the angle of minimum deviation the incident and emerging pencils make the same angle with the faces of the prism, at which they respectfully enter and leave the glass. Hence a second prism like the first stands in the same relation to the emerging beam in which the first stands to the incident beam. If then, after the first prism has been adjusted at the angle of minimum deviation a second prism be applied against the wheel at the side of the first, by moving the prism slightly to one side or the other, it will be easy to find a position, in which this prism also is at the angle of minimum devia-

tion, moving of course the prism on the plate without disturbing the position of the plate itself. In like manner other prisms may be added until the required number is obtained. (In the Cambridge spectroscope there are nine glass prisms of 45°, as shown in fig. 4.) This adjustment has only to be made, however, once for all, since when the prisms are adjusted they are fastened to a very thin, flexible brass ribbon, which, passing through a box at the back of each prism, is there secured by clamping screws. The ends of this ribbon, moreover, are attached to a small brass drum, which, being wound up by an ordinary clock spring, draws the chain of prisms tightly around the conical wheel, and keeps them always in place. By tracing the path of a ray of homogeneous light through a series of similar prisms, as is shown in fig. 4, it will be found that the path of the ray within the prisms is always tangent to the same circle, provided that it passes through all under the conditions of least deviation. Assuming, then, that the distances between the prisms are invariable, as they must be when the prisms are fastened to a brass ribbon as just described, it will be evident from a moment's reflection that the greater the refrangibility of the given ray the less must be the diameter of the circle, around which the prisms should be arranged in order that the ray may pass under the required conditions, and, knowing the dimensions of the prisms as well as the index of refraction and dispersive power of the glass, it is easy to calculate approximatively what the diameter should be in a given case. The dimensions of the conical wheel A, fig. 2, were thus determined—the largest diameter, 9½ inches, corresponding to the extreme red, and the smallest diameter, 8½ inches corresponding to the extreme violet rays of the solar spectrum. In order to facilitate the adjustment a series of lines were engraved encir-

Fig. 4.



cling the wheel at equal distances from each other and numbered from 1 to 12.

Having described the construction of the instrument it will now be easy to understand the method of using it. Let us suppose that the object is to measure the angle of minimum deviation of the blue ray of the strontium spectrum. By examining any chart of the spectra of the chemical elements it will be found that this line is situated roughly at somewhat less than two-thirds of the distance from A to H. If, then, we turn the conical wheel until the pins of the prisms all rest against the line marked 7, we shall have approximatively the true position. We then adjust the collimator with reference to the first prism exactly as before described for a single prism. Turning then the upper plate so as to remove the prisms out of range, we bring the observing telescope into collimation with the collimator, as also before described, when on reading off the limb we have the starting point for our measure. We next turn the plate and move the telescope until the spectrum appears in the field, and carefully bring the blue line to coincide with the vertical wire at the position of minimum deviation. We now raise or lower the conical wheel and notice if in this way the angular deviation is diminished, and leave the wheel in the position where the minimum is reached. It now only remains to again read the limb when the difference of the two readings subtracted from 360° will give the angular deviation required.

When near the position of minimum deviation a large motion of the conical wheel produces only a slight motion of the image, so that after a table has been made giving the position of the wheel for a few of the marked lines of the spectrum it is always possible to bring the wheel at starting to the desired point. Moreover, the fact that when near the position of minimum deviation the position of the image is affected so slightly by a small change in the position of the prisms, renders it possible to make all the adjustments required with exceeding rapidity and accuracy.

In order to test the accuracy of our method we have made several determinations of the minimum deviation of the line D, and although between each determination the whole apparatus was completely dismounted, the value obtained was in all cases 267° 37′ 50″.[1] It will be remembered that the sum of the angles measured on each prism separately at the center of the plate, as given on page 309, is precisely the same (267° 37′ 50″) and the sum of those measured on the edge of the plate (267° 37′ 30″) only differs from this by 20″.

When it is not important to use absolutely the whole aperture of the prisms it is not necessary to change the position of the collimator in passing from one part of the spectrum to an-

[1] As the mean of the two lines.

other. If we adjust the collimator as above described, when the prisms rest against the middle circle on the wheel, the whole spectrum can be passed under review with great rapidity without any further change of the collimator, and each point seen under the condition of minimum deviation. When, however, on account of the feebleness of the light it is important to use the whole aperture of the prisms, a slight gain can be obtained by readjusting the collimator at the extreme points of the spectrum. In making the measurements described in this paper, an important advantage is gained in keeping the position of the collimator fixed; for if its position is changed, the point to which the angular measurements are referred is changed also, and must be determined anew. If however the arms, to which the telescopes are attached, are so arranged with a sliding motion that both the collimator and the observing telescope may be moved parallel to themselves without altering their relative angular position, the whole aperture of the prisms may at any time be used, and nevertheless all the measurements referred to the same point on the graduated limb.

Besides the set of glass prisms the Cambridge spectroscope is also provided with a set of sulphid of carbon prisms, which have been previously described in this Journal. They are mounted on a separate plate with a separate wheel of the proper dimensions and are arranged in all respects like the glass prisms above described. The plates are provided with handles so that one battery of prisms may be quickly lifted off from the instrument and the other put in its place. But although the liquid prisms are valuable on account of their great dispersive power in bringing out faint lines, especially in the more luminous portions of the spectrum, yet their use is very restricted. One difficulty arises from the immensely rapid change of the index of refraction of sulphid of carbon with the slightest change of temperature. We have noticed within half an hour on a summer's day a change of 8′ in the angle of minimum deviation of a single sulphid of carbon prism of 45°, although the temperature of the room had only in the meantime changed eight tenths of a Centigrade degree. The temperature of the prism undoubtedly changed much more than this; but when we remember that the variation thus produced would amount to over one degree for the nine prisms, it will be seen that they must be useless for any purposes of direct measurement. Again, sulphid of carbon is far less transparent than glass to the more refrangible rays of the spectrum, and lastly, a slight change of temperature in the observing chamber produces at once currents in the liquid, which are fatal to good definition. Nevertheless under the best conditions, we have found that sulphid of carbon prisms define as well or even better than glass. The instrument

described in this paper, with the exception of the glass prisms, was made by Messrs. Clark & Sons of Cambridgeport, and we would here especially express our indebtedness to Mr. George Clark for his great ingenuity in planning and executing the mechanical details. We reserve for another article an account of the results of our measurements.

[From the Proceedings of the American Academy of Arts and Sciences, Vol. VII., January, 1866.]

ON THE AQUEOUS LINES OF THE SOLAR SPECTRUM.

By JOSIAH P. COOKE, Jr.

A careful examination of the solar spectrum, continued during several months with the spectroscope described in a recent article of the American Journal of Science,* has led me to the conclusion that a very large number of the more faint lines of the solar spectrum, hitherto known simply as *air* lines, are due solely to the *aqueous vapor* of our air, and hence that the absorption of the luminous solar rays by the atmosphere is at least chiefly owing to the aqueous vapor which it contains.

The appearance of the Fraunhofer's line D, seen under precisely the same conditions, but with increasing quantities of aqueous vapor in the atmosphere, is shown in Figures 1, 2, 3, and 4. The D line is selected, because being a favorite test object for the spectroscope, its general appearance is well known to all observers. But even more marked changes than those here illustrated have been noticed in other, although chiefly in contiguous, portions of the solar spectrum.

These changes attracted my attention from my earliest observations with the spectroscope; but with my first instrument, and the bisulphide of carbon prisms then employed, it was almost impossible to eliminate the effects which might be caused by the variations in the condition of the instrument itself; and as these were known to be very great, it was possible that they might account for all the variations observed. With the improved instrument, however, just referred to, absolute constancy of action is obtained, and all merely instrumental variations avoided.

A peculiar condition of the atmosphere gave the first clew as to the

* American Journal of Science and Arts, Vol. XL., November, 1865.

cause of the changes under consideration. The weather on the 17th of November, 1865, at Cambridge, Massachusetts, was very unusual even for that peculiar season known in New England as the Indian Summer. At noon the temperature on the east side of my laboratory was 70° F., while the wet-bulb thermometer indicated 66°, showing an amount of moisture in the atmosphere equal to 6.57 grains per cubic foot. At the same time the atmosphere was beautifully clear, and the sun shone with its full splendor. I have never seen the aqueous lines of the spectrum more strongly defined than they were on this day; and the total number of lines visible in the yellow portion of the spectrum was at least ten times as great as are ordinarily seen. The appearance of the D line on that day is shown in Fig. 4. Between the two familiar broad lines D_1 and D_2 there were eight sharply defined lines of unequal intensity, which is only very imperfectly represented by the woodcut. In addition to these, on the more refrangible side of the space, between the two D lines, there was a faint but broad nebulous band, barely resolvable into lines of still lower magnitude.* It is impossible to represent this band accurately with a woodcut; and the shaded broad band marked κ on the right-hand side of Fig. 4 only serves to indicate its position and approximate breadth.

The 26th of December was also a warm day for the season, with a brilliant sun. At one oclock, P. M., the dry-bulb thermometer marked 55°, the wet-bulb 50°, and hence the amount of moisture in the atmosphere was 3.76 grains per cubic foot. The appearance of the D line at this time is shown in Fig. 3. Two of the lines, η and θ, and the nebulous band κ, seen on the 17th of November, were invisible, and moreover the group of three lines δ ϵ ζ on the left-hand side of the figure were only just within the limits of visibility.

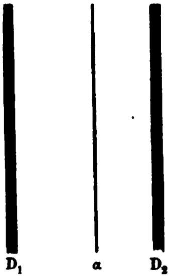
On the 25th of December only two lines were visible within the D line, marked α and β, in Fig. 2, and the last of these was quite faint. The temperature at the time of observation was 46°; the wet-bulb thermometer indicated 40°, and the amount of moisture in the air was 2.42 grains per cubic foot. The sky was clear and the sun brilliant. Lastly, on January 5th, 1866, one of the clear cold days which are so common in our climate during the winter, only the single line α was visible within the D line, as is shown in Fig. 1. At the time of

* We use this word in the same sense in which it is used by astronomers with reference to the fixed stars.

January 5th, 1866.

Temperature 10° F.
Dew-Point 1°.5 F.

Fig. 1.

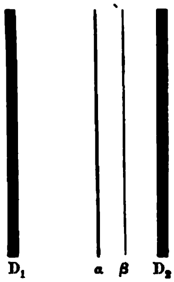


Weight of vapor in 1 cubic foot of air, } **0.81 grs.**

December 25th, 1865.

Temperature 46° F.
Dew-Point 33°.4 F.

Fig. 2.

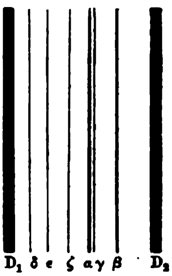


Weight of vapor in 1 cubic foot of air, } **2.42 grs.**

December 26th, 1865.

Temperature 55° F.
Dew-Point 46°.5 F.

Fig. 3.

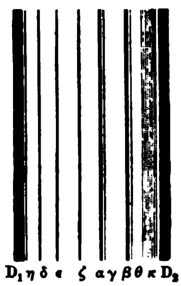


Weight of vapor in 1 cubic foot of air, } **3.76 grs.**

November 17th, 1865.

Temperature 70° F.
Dew-Point 64°.0 F.

Fig. 4.



Weight of vapor in 1 cubic foot of air, } **6.57 grs.**

observation, near noon, the dry-bulb thermometer marked 10°, the wet-bulb 9°, and hence the amount of moisture in the atmosphere was only 0.81 of a grain per cubic foot. The sun, however, was as brilliant as in either of the previous cases. The D line also appeared as in Fig. 1 on the 8th of January, 1866, when the thermometer at noon stood at 10° below zero Farenheit, and when the barometer attained the unexampled height of 31 inches.

The above figures have been drawn so as to show, as nearly as possible, the relative intensity of the different lines under different atmospheric conditions. As no accurate means of making the comparison are yet known, I was obliged to depend upon my eye alone, and small differences at different times of observation may easily have escaped my notice. Indeed, I should have been liable to great error were it not for the fact that one of the lines within the D line, marked α in all the figures, does not vary in intensity, and served as a constant standard in making the observations. This is the only line which is given by Kirchoff in his chart of the solar spectrum between the two D lines, and it is referred by him to the Nickel vapor,—as the D lines themselves are to the Sodium vapor, in the sun's atmosphere. It is an undoubted solar line, and has been drawn with the same strength in all the figures in order to show that it is invariable.

With a very dry atmosphere the line α is the only one which appears within the D lines, as shown in Fig. 1. With a slightly greater amount of vapor the line β makes its appearance. As the amount of vapor continues to increase, this line becomes more and more prominent, until at last, as shown in Fig. 4, it is even more intense than the line α. A careful comparison of these two lines might indeed serve as an approximate measure of the amount of vapor in the atmosphere; and a series of comparisons made under the same conditions at different heights would give data for determining the law according to which the amount of vapor decreases with the elevation above the sea level.

All the aqueous lines change in intensity like the line β. They are first seen very faintly when the amount of vapor in the air reaches a definite point, varying for the different lines, and gradually gain in intensity as the amount of vapor increases. Thus the group of three lines $\delta\ \epsilon\ \zeta$ do not appear in Fig. 2, are barely visible in Fig. 3, but become very marked in Fig. 4.* The lines η and θ and the nebulous band κ do

* With an increasing quantity of vapor in the atmosphere the line γ of Fig. 3 is seen before the group of lines $\delta\ \epsilon\ \zeta$, and an intermediate figure between 2 and 3 might be given showing only the lines $D_1\ \alpha\ \gamma\ \beta\ D_2$.

not appear until the air is very moist; and even when it contains 6.57 grains of vapor per cubic foot, they are still very faint. Under yet more unusual atmospheric conditions they will undoubtedly become more intense, and we shall then probably be able to completely resolve the nebulous band and count the lines of which it consists.

It is hardly necessary to repeat, that the examples here given are selected from a large number of observations. During the cold dry weather of winter the appearance of the D line is uniformly as shown in Fig. 1, the line β only occasionally appearing when the atmosphere becomes more moist. During the warm weather of summer, when the absolute amount of moisture in the air is in almost all cases greater than in winter, the appearance of the D line is as uniformly that shown in Fig. 3. It is only very rarely in the dry climate of New England, even during the summer, that all the lines shown in Fig. 4 are visible; and, as already stated, I never saw them before so sharply defined as on the 17th of November last.

Several conditions must evidently concur in order that the aqueous lines should be developed in their greatest intensity. In the first place, the air must be charged with vapor not only near the surface of the earth, but also through a great height of the atmosphere. Local causes might greatly increase the amount of moisture in the lower strata of the atmosphere, and affect powerfully the hygrometer, which would not, to the same extent at least, influence the indications of the spectroscope. In the second place, other things being equal, the intensity of the aqueous lines must be strengthened by increasing the length of the path of the sun's rays through the atmosphere, and this is the longer the lower the altitude of the sun. But then, again, the intensity of the light has such an important influence on the definition of the lines, and the slightest haze in the atmosphere so greatly impairs their distinctness, that I have generally found that the aqueous lines are seen best when the sun is near the meridian. Hence, with an equal amount of moisture in the atmosphere, the late autumn may be a more favorable season for seeing the aqueous lines than the summer; for then not only must the solar rays, when most brilliant at noon, traverse a greater extent of air, but moreover the atmosphere at this time is usually clearer, and the reflected beam of light which enters the spectroscope is at times more brilliant than when the sun attains a higher elevation and the light is reflected under less favorable conditions.

In the examples cited above, the comparisons were made under as

nearly as possible the same conditions, so as to eliminate all causes of variation except the one under consideration. Days were selected when the atmosphere was perfectly clear, and the sun's light, so far as I could judge, equally brilliant. Moreover, the position of the spectroscope and mirror remained unchanged during the whole time. This mirror, which is used for reflecting the sun's light upon the slit of the spectroscope, is so arranged that it can be turned into any position by the observer while his eye is at the eye-piece of the spectroscope, and it was always carefully adjusted at each observation to the position of best definition. The manipulation of the mirror is fully as important in the use of the spectroscope as it is in microscopy.

It will be of course understood that the power of developing these faint aqueous lines depends very greatly on the optical capabilities of the spectroscope, and that the figures here given are relative to the instrument used in the observations. This instrument has been fully described in the article already cited. It is sufficient for the present purpose to state that it is provided with nine flint-glass prisms * of 45° refracting angle, which bend the rays of light corresponding to the D line through an angle of 267° 37′ 50″, and that corresponding to the H_1 line through an angle of 280° 42′ 20″, when each passes through the prisms at the angle of minimum deviation. The dispersive power, therefore, of the instrument for these two rays is equal to 13° 4′ 30″, and the rays corresponding to the two D lines are separated 1′ 10″. The object-glasses of the two telescopes of this spectroscope are 2¼ inches in diameter, and have a focal length of 15½ inches, and lastly the size of the prisms, and of the various parts of the instrument, is adapted to these dimensions. With a more powerful instrument a larger number of aqueous lines would be seen under the same atmospheric conditions. The Cambridge instrument has a set of sulphide of carbon prisms which disperse the light nearly twice as much as the flint prisms. The sulphide of carbon prisms are very variable in their action; but, under the best conditions, they might show the D line as in Fig. 3, when with the flint prisms it would appear as in Fig. 2.

The facts stated in this paper fully account for the discrepancies in the representations which different observers have given of the D line.

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* These prisms were furnished by the American Academy from the income of the Rumford Fund, appropriated for investigations on light and heat. See Proceedings of the American Academy, Annual Meeting, May 24th, 1864.

Some time since, Mr. Gassiot, of London, gave in the Chemical News a representation of the D line as seen with his instrument, showing several lines in addition to those seen by myself and other observers. On visiting the Kew observatory, in the summer of 1864, I was surprised to find that this instrument was less powerful than the one I was then using; and I also learned that these lines were only seen on a single occasion. The moist climate of England is the evident explanation of the additional lines.

As I stated at the first of this paper, the D line has been selected simply to illustrate a general truth. The development of aqueous lines in contiguous portions of the spectrum is even more marked than in the exceedingly limited portion here represented. Indeed, as has been already intimated, the number of these lines seen in the yellow region of the spectrum, on the 17th of November, was at least ten times as great as that of the true solar lines. That part of the yellow of the spectrum which lies on the more refrangible side of the D line, and in which during dry weather only a comparatively few lines can be distinguished, was then as thickly crowded with lines as the blue or the violet, but the lines were of course far less intense.

Professor Tyndal, of London, has shown by a remarkable series of experiments with the thermo-multiplier, not only that aqueous vapor powerfully absorbs the obscure thermal rays, but also that the elementary gases of the atmosphere exert little or no action upon them. I have endeavored to establish in this paper, from direct observations with the spectroscope, a similar truth in regard to the luminous rays. It has been estimated by Pouillet and others that about one third of the solar rays intercepted by the earth are absorbed in passing through the atmosphere; and it now appears that aqueous vapor is a most important, if not the chief, agent in producing this result. It is impossible, however, from any data we yet possess, to determine how great a power of absorption is exerted by the oxygen and nitrogen gases, which constitute the great mass of our atmosphere. I have shown that a very great many, and I have no doubt that almost all, the lines hitherto distinguished as air lines are simply aqueous lines; but it is very difficult to distinguish atmospheric lines from the true solar lines, and our knowledge of the first is as yet very incomplete. It still remains to make careful comparisons throughout the whole extent of the spectrum, before we can absolutely determine the relative absorbing power of the different constituents of our atmosphere.

One other inference from the facts here developed is worthy of notice before closing this paper. It has been for some time suspected that the blue color of the sky was in some way connected with the vapor in the atmosphere; and it is a fact of common observation, that this color is more intense during the moist weather of summer than during the more dry weather of winter. The distribution of the aqueous lines through the solar spectrum not only confirms the opinion previously entertained, but also points to the cause of the color. So far as my observations have extended, the aqueous lines are almost wholly, if not completely, confined to the more refrangible portion of the spectrum. Here they are found in vast numbers, and I am not positive that they exist anywhere else. If, then, the aqueous vapor absorbs most powerfully the yellow and red rays of the spectrum, the blue color of the sky is the necessary result. The color is therefore due to simple absorption, and not to repeated reflections from the surface of drops of water, as some physicists have supposed.

As can readily be seen, the aqueous lines of the solar spectrum present a very wide field for investigation, but one which can only be cultivated under peculiar atmospheric conditions. This paper is only intended to open the subject. I hope to be able to continue the study on every favorable opportunity, and shall take pleasure in communicating any future results to this Academy.

CAMBRIDGE, January 9, 1866.

SCIENTIFIC INTELLIGENCE.

I. PHYSICS.

1. *The Radiometer.*—A large number of papers on this subject have appeared during the past few months. Several of these have been published in Poggendorff's Annalen, and of the rest, excellent abstracts are given in the "Beiblätter" to that journal. They give evidence of a very great amount of ingenuity expended in devising experiments to test the theory of this very remarkable instrument, and they show how easily experimental evidence may be misinterpreted in support of an assumed theory when the phenomena in question are liable to be modified by many adventitious circumstances. Five theories of the radiometer have found prominent and weighty advocates. The first regards the motion of the instrument as a *direct* effect of radiation. The second refers it to electrical action. The third to convection currents. The fourth to the emission of material particles from the vanes or the walls of the instrument. The last finds in the apparatus simply a new heat engine, and sees in the motion a simple result of the difference of temperature of the parts, wholly in accordance with the modern mechanical theory of heat.

When this motion was first discovered it seemed to be a direct mechanical effect of radiation, and there were not wanting ingenious speculations to show how the force exerted by the waves of the luminiferous ether might be resolved so as to produce such an effect. It is to be remarked, however, that Mr. Crookes, to whom we owe the discovery, did not indulge in such speculations, and, as he says, aimed to keep himself unbiased by any theory while he accumulated the facts upon which a satisfactory explanation might be based. But the very name *radiometer* implied, and the whole tenor of his published papers have certainly justified, the common opinion that, until very recently, he regarded the phenomena—he had so admirably developed—as a *direct effect* of radiation, and not, as he now thinks, a secondary result depending on differences of temperature, which may be produced by radiation or by other means. Hence, several experimenters have labored to show that in the motion of the little wheel of the radiometer the reaction was exerted not against anything independent of the instrument, but against the enclosing walls of glass. The early experiments of Mr. Schuster* on this point were very convincing. He hung the whole instrument by a delicate bifilar suspension, and found that while the vanes were revolving under the action of a beam from an oxyhydrogen lamp, the glass bulb also turned slightly in the opposite direction. Soon after M. Salet† constructed a very ingenious apparatus in which this reaction was made to turn a mica disk; and very recently, M.M. Bertin et

* Philosophical Magazine, Nov., 1876.
† Comptes Rendus, Nov. 20, 1876.

Garbe* have published an interesting paper, in which they show by careful measurements that the reaction of the glass bulb fully accounts for the motion of the wheel; and their investigation may be regarded as finally disposing of the radiation theory, by proving that the motion of the wheel of the radiometer is wholly caused by forces which act within the glass bulb.

The electrical theory has never had many supporters. It is, however, defended in two recent articles by J. Delsaulx† and W. de Fonvielle.† In opposition it is urged that no distribution of statical electricity could maintain a constant motion,‡ and further, Mr. Crookes§ cites an experiment of Mr. Cromwell F. Varley, with an apparatus so arranged that the electrical condition could be tested with a delicate electroscope; when not the slightest trace of electrical excitement could be detected, although the motion of the wheel was regularly maintained.

The convection theory has been recently advocated by F. Neesen,‖ who describes a number of experiments which he thinks indicate that the wheel of the radiometer is moved by the gas currents occasioned by the rising or falling of the residual air particles as they are warmed or cooled, at the surfaces of the vanes or of the enclosing glass walls. But the effects he obtains by placing similar wheels unsymmetrically under the receiver of a mercury pump, do not, as it seems to us, necessitate his explanation, and moreover the distinction between the effect of convection currents and the peculiar motion of the radiometer is strikingly marked in many experiments which have been elsewhere described, the one passing into the other at a certain degree of exhaustion.¶

The emission or evaporation theory appears to have originated with Mr. Osborne Reynolds. It was later maintained by Govi,** and recently it has formed the subject of an extended article—in three parts—by F. Zöllner.†† This theory refers the motion to an alternate emission and absorption of material particles—determined by variations of temperature—at the several surfaces, between which the moving forces in the radiometer are exerted. The particles thus emitted may be either those of aeriform substances adhering to or occluded by the solid materials of which the instrument is made—as Reynolds supposed—or it may be, as Zöllner suggests, that these solids themselves *evaporate* slowly into the vaccuous space. Leaving, however, such questions in abeyance—as these physicists prefer,—there is no doubt that the general order of the phenomena might be explained if the assumptions which the emission theory requires could be accepted; but on the other hand, the phenomena which Zöllner adduces in support of his view, may be,—for the most part at least—fully as well explained by the more general mechanical theory of heat. Zöll-

* Annales de Chim. et de Phys., [V] xi, 45, Mai, 1877.
† Beiblätter, i, 170. ‡ Beiblätter, i, 329. § Pogg. Ann., clx, 143.
‖ Compare Zöllner, Pogg. Ann., clx, 459. ¶ Proc. Royal Soc., 1874, June 18.
** Pogg. Ann., clx, 154, 296 and 459. †† Comptes Rendus, lxxxiii, 1.

ner endeavors to show* that the mean path of the molecules of the residual gas in the bulb of the radiometer, when it is in the condition of maximum sensitiveness, is not large enough to fulfill the conditions which the mechanical theory requires. On the other side, Crookes† has obtained motion or the reverse, under conditions which certainly appear incompatible with the emission theory. Moreover, the very fact which appears to have been well established by several observers, that, with a certain degree of exhaustion, different for different gases, a point of maximum sensitiveness is reached, and that on further exhaustion the sensitiveness rapidly diminishes, seems to us,—especially when viewed in connection with the experiments just referred to—fatal to the emission theory.

The last theory we have to consider is, as we have said, but a phase of the mechanical theory of heat. The application of the now well known principles of molecular dynamics to the explanation of the new phenomena is said to have been first suggested by Mr. Johnstone Stoney.† Similar views were also very early expressed by Professors Tait and Dewar.‡ More recently they have been adopted by Mr. Crookes,§ and are now very generally accepted by physicists.

According to the mechanical theory of heat, the molecules of any gas which rebound from a surface with a temperature—that is, with a velocity—different from that with which they struck, must cause a recoil, and this must be the general case whenever the temperature of the surface is different from that of the mass of the gas. Unless, however, the density of the gas is exceedingly small, the rebounding molecules almost at once collide with their neighbors, and are immediately driven back against the same surface. Thus the change of temperature merely affects a very thin layer of molecules near the surface, and these are only slowly displaced by convection. In such an atmosphere, the vanes of a radiometer, for example, with the adjacent molecules, are parts of one system, and, by a well known mechanical law, no motion of the system as a whole can be produced by any action between its parts; but when the medium becomes so rare that the mean path of the molecules is comparable with the dimensions of the enclosing vessel, so that some of the molecules, rebounding from the vanes of the radiometer, may even reach the opposite walls, then of course a force is exerted between the opposing surfaces, and the now familiar motion of the wheel is the result. The radiometer is then simply a heat engine in which the action takes place between two surfaces of different temperature, the heater and the cooler of the engine. As such a difference of temperature may be maintained in a great variety of ways, so the apparatus admits of a great number of modifications. Moreover, it is obvious that

* Pogg. Ann., clx, 305. † Beiblätter, i, 167 and 330. ‡ Nature, July 15th, 1875.
§ Philosophical Transactions, vol. clxvi, p. 375, in postscript dated June 17, 1877. See also Mr. Stoney's papers. Phil. Mag., V, i, pp. 177–182, 305–314, (1876).

when, as in most cases, the difference of temperature is the result of radiation, very irregular effects may be produced by the different absorbing or radiating power of the surfaces for the various rays of the spectrum, and also by similar differences in the diathermancy of the glass envelope. It is not surprising then that some of the phenomena which have been met in the course of the numerous investigations already made on this subject, should have been so difficult to trace. There can be no question, however, that the general order of the phenomena is fully explained by this theory. In the postscript just referred to, Mr. Crookes writes, "Twelve months' research, however, has thrown much light upon these actions, and the explanation afforded by the dynamical theory of gases makes, what was a year ago obscure and contradictory, now reasonable and intelligible."

It does, however, still remain to show that the dynamical theory of heat is quantitatively as well as qualitatively confirmed by the new phenomena. The necessary measurements unfortunately present very great experimental difficulties, and the data thus far obtained can only be regarded as rough estimates, and for this reason we do not attach much importance to the criticisms of Zöllner already referred to. Among the results bearing on this question recently obtained, the most interesting are the following.

Of course, according to the theory in question, there would be no motion whatever in an absolute vacuum, and hence, as we have intimated, the molecular pressure on the vanes of a radiometer ought to reach a maximum effect with a certain limited degree of exhaustion. Moreover, as the length of the mean path of a molecule, other things being equal, depends on the molecular weight,—the lightest molecules having the greatest extent of motion under the same conditions,—it also follows that the limit just mentioned should be sooner reached in the residue of a light than in that of a heavier gas. In accordance with these anticipations, Mr. Crookes has found that while with hydrogen the maximum effect is reached at a tension of about 0·0532 millimeters, it is not obtained with oxygen until the tension is reduced to 0·0228 millimeters, or less than one half of the previous value. In an ordinary radiometer, according to the same experimenter, the tension of the residual air is about 0·19 millimeters, but he has succeeded in reducing it to 0·0076 millimeters, and then the velocity of the motion was only one-tenth of the maximum. Still later he states that by heating the bulb to 300° during the exhaustion, he has been able to reduce the tension to one or two millionths of an atmosphere, and that he can most readily secure the condition of greatest sensitiveness by first pushing the exhaustion to the utmost limit of the power of his apparatus,* and then with the aid of a peculiarly constructed cock allowing gas to enter until the proper tension is reached. By

* Crookes has obtained these later results with a new form of the Sprengel pump, contrived by C. H. Gimingham, and an ingenious application of the mercury gauge to measuring low tensions, made by McLeod. Full descriptions of these new forms of apparatus, with figures, will be found in the Beiblätter, i. 175.

using vanes of mica previously rendered anhydrous by ignition and working with hydrogen, he has thus succeeded in constructing a radiometer of such sensibility that it moved under the sole influence of the moon's rays. The results of Finkener on the point of maximum sensibility in different gases confirm those of Crookes, the two series of measurements agreeing as nearly as could be expected, and all these results—with yet others—have been collected in a very interesting paper recently published by M. Bertin.* No one has yet succeeded in pushing the exhaustion so far beyond the point of maximum effect that the radiometer became again insensible to radiation, nor was that to be expected.

It is another consequence of the dynamical theory of gases that a radiometer with a small bulb ought to be more sensitive—under otherwise like conditions—than one with a large bulb, and this also has been fully realized by Mr. Crookes.† Quite recently, Stoney and Moss‡ have published some preliminary results of an investigation, in which they propose to compare the molecular pressure between the "cooler" and "heater" in this new form of heat engine at different distances and with various gas residues, and under varying conditions of tension, temperature, etc. The investigation was begun soon after the publication of Stoney's original communication to the Phil. Mag., March, 1876, and is not yet completed. They give a description of their apparatus, and they call the reaction exerted between the cooler and heater in the radiometer and all similar instruments, "Crookes' Force." We must refer to their paper for details which appear to authorize the conclusion that in a residue of hydrogen having a tension of five millimeters, the molecular pressure, or "Crookes' Force," is sensible at a distance of at least ten millimeters.

Again, although the molecular pressure we are considering must in general conform to the well known laws of hydrostatics, like the tension of the atmosphere, yet the mechanical theory of gases would lead us to anticipate certain striking differences of effect resulting from the great amplitude of the molecular motion in an extremely rarified medium. Thus the tension of the atmosphere does not move the vanes of an anemometer; but a wind does. And in a somewhat similar way—when the wheel of a radiometer is made like that of the anemometer—the resultant of the recoils due to the acceleration of the rebounding molecules will be greater on the convex than on the concave surface of the cups, although being made of thin metal plate, the temperature of the two surfaces must be essentially the same. Such effects have been studied both by Crookes§ and by Zöllner.‖

It is greatly in favor of the view of the subject last presented that it does not invoke a new agency or exaggerate an old one to explain the new phenomena; but it is merely a new phase of an already well established theory, which, by thus readily marshalling the new phenomena, becomes more firmly established. Indeed, to

* Annales de Chimie et Physique, V, x, 396, Mars, 1877. † Beiblätter, i, 165.
‡ Beiblätter, i, 318, No. 6; also Proc. Roy. Soc., xxv, 553.
§ Beiblätter, i, 169. ‖ Pogg. Ann., clx, 159.

those who accept this theory the radiometer becomes an instrument of the very highest interest, affording as it does, another and very striking manifestation of molecular motion. Moreover, when we shall be able to overcome the experimental difficulties so as to estimate with certainty the force exerted under determinate conditions, we may hope to obtain by its aid a direct measure of absolute molecular magnitudes.

We may be permitted to add to this notice a brief account of a few experiments made with the radiometer at Cambridge in the spring of 1876, soon after the instrument had been received from Europe. We became at once greatly interested in the new phenomena, and with the aid of a skillful glass blower made more than a hundred instruments of different patterns. Our experience led us at once and independently to the theory of its action now generally received; but although we sustained this view in our college lectures, in a communication to the American Academy, and in a popular article in the Boston Daily Advertiser, we did not otherwise publish our results, because we felt that the field had been in a measure preëmpted by the discoverer of the phenomena, who was then investigating the subject, and who, we felt sure, must come at last to the same conclusions which we had reached. Our results can now add nothing to the strength of the theory, which has been since so well worked out by Mr. Crookes, but two of the experiments have never been—so far as we know—described before, and being so simple that they can be easily repeated in any physical cabinet, a description of them, even at this late day, may have an interest for teachers of physics.

We first experimented with a common radiometer having mica vanes blackened on one side, which we placed in a beam of parallel rays from an oxyhydrogen lantern; and having satisfied ourselves—by using an alum cell—that the rays acted chiefly at least through their heating and not their luminous power, we made at once this experiment. We placed an opaque screen near the radiometer so that only the blackened faces should be exposed as the wheel turned the vanes into the beam of light. We then counted with a stop watch the number of seconds which passed during ten revolutions. We then in a similar way exposed only the uncoated faces; when the wheel continued to turn in the *same direction*, although much more slowly than before. Again we counted the revolutions. Lastly we counted the revolutions while the beam shone on both sides of the vanes as usual. We repeated the experiment several times, and were surprised at the remarkable constancy of the results. They were as follows:

	Time of ten revolutions.	Revolutions in same time.
With both faces exposed	8"	319
With lampblack faces alone exposed	11"	232
With mica faces alone exposed	29"	88

and it will be noticed that 88+232 equals very nearly 319. Now any uniform force whatever, acting from without and at once on the two arms of a lever like these vanes, must act differentially and not concurrently, as here. Hence the reaction which causes

the motion must take place between the parts of the instrument itself; or else we are driven to the most improbable alternative that lampblack and mica should have such a remarkable selective power that the impulses, then supposed in some mysterious way to be imparted by the beam of light, could exert a repulsive force at one surface and an attractive force at the other. Were there, however, such an improbable effect, it must be independent of the thickness of the mica vane; while on the other hand, if, as seemed to us most probable, the whole effect depended on the difference of temperature between the lampblack and the mica, and if the light produced an effect on the mica surface only because the mica plate being diathermous to a very considerable extent, the lampblack became heated through the plate more than the plate itself, then it would follow that if we used a thicker mica plate, which would of course absorb more of the heat, we ought to obtain a marked difference of effect. Accordingly we repeated the experiment with an equally sensitive radiometer—which we made for the purpose with comparatively thick vanes; and with this the effect of a similar beam of light on the mica surface was absolutely null, the wheel revolving in the same time whether these faces were protected or not. It was now an obvious step to heat the glass of the bulb independently of the vanes in order to see if under these circumstances we should not obtain a reverse action. This was easily effected both by warming the glass over a lamp and also by placing the bulb tangentially toward the beam from the lantern, so that it heated the glass without striking the vanes of the wheel. We thus easily obtained the now familiar reverse motion, but which was to us a new discovery. We therefore felt ourselves justified in speaking of the radiometer, as we did in the communications referred to, as a heat engine, of which, when moving in the ordinary way, the lampblack surface of the vanes is the "heater" and the inner surface of the glass bulb the "cooler," but in which these conditions could be reversed as just described. And then the parallel with the steam engine, which we drew, suggested the extension of the dynamical theory of gases to include the new phenomena almost in the very words used above. Moreover, while exhausting the large number of radiometers of which we have spoken, we noticed variations in the effects produced, caused by differences in diathermancy between crown and flint glass, and were thus led to realize what an important part this property of matter played in these phenomena. We also observed that the larger the bulb to the greater degree must the exhaustion be pushed in order to obtain equal sensitiveness. We further found that the same sensitiveness could be more readily obtained with a residue of hydrogen than with one of air, and we recognized plainly that there was with each instrument a point of maximum sensitiveness which could not be exceeded. We had also devised an apparatus for measuring the force exerted under determinate conditions, but our experiments were brought to an end by the sudden death of the only skillful glass blower in our neighborhood.

Soon after these experiments, Mr. B. O. Peirce, now assistant in the Physical Laboratory of Harvard College, made the following striking comparison of the relative effects produced by a large variation in the same radiant source on a radiometer and a thermopile. He used a large Bunsen burner provided with an air valve, so that the non-luminous could be at once changed to a luminous flame. He placed the burner midway between the radiometer and the pile which were about one meter apart. The radiometer was protected from the radiation of surrounding objects by a tin case, blackened on the inside, except where a circular aperture admitted the rays of the lamp and where the reflecting surface of the cover set obliquely enabled the observer to count the revolutions of the radiometer wheel. In front of the thermopile was placed an opaque screen, having an aperture of the same size as that of the radiometer case, and also a thin plate of glass to correspond to the glass of the radiometer bulb. Beginning with the non-luminous flame, Mr. Peirce counted the number of turns of the wheel of the radiometer in a minute, and also took the readings of the galvanometer; then, after rendering the flame luminous (by shutting the air valve), the same observations were repeated. A comparison of the similar values gave, of course, the relative radiation of the non-luminous and the luminous flame as measured by the radiometer on the one side and the thermopile on the other.

	Radiometer.	Thermopile.
1.	0·343	0·287
2.	0·309	0·380
3.	0·248	0·283
4.	0·267	0·325
5.	0·277	0·350
6.	0·367	0·250
7.	0·394	0·304
Mean,	0·315	0·311

While, therefore, there was quite a large variation between the several observations, as might be expected with such a variable source as a Bunsen flame, yet the close agreement of the averages showed conclusively that with the radiometer, as with the thermopile, the effect caused by the rays of light must arise solely from the change of temperature thus produced. It will be noticed that—as measured by either instrument—the radiation of the luminous flame produced only about three times the effect obtained from the non-luminous flame; while a photometric comparison made at the same time showed that the illuminating power of the first was at least a thousand times greater than that of the second. Two separate experiments gave 1080 and 1079 times greater respectively.

In this notice we have been able to refer to only a few of the salient points presented in recent articles on the radiometer, and it will of course be understood that our limits prevent us from even alluding to a large number of other very interesting observations bearing on the subject. J. P. C., JR.

Newport, August 3d, 1877.

[From the American Journal of Science, Vol. XIX, April, 1880.]

Notice of Berthelot's Thermo-Chemistry; by J. P. Cooke, Jr.

The new work of M. Berthelot, entitled "Essai de Mécanique Chimique fondée sur la Thermo-chemie," presents for the first time in a systematic form the results accumulated during the past ten years from one of the most fruitful fields of investigation ever opened to the chemist. The book supplies a most important want, for the details of the work—published in numerous separate papers rapidly following each other in the chemical journals—have been almost unintelligible, except to those who have followed the investigation from the beginning, and no connected statement of the general principles involved was accessible to the student. The work in this new field has been done almost wholly by two investigators, Berthelot, of Paris, and Thomsen, of Copenhagen. Guided by different theoretical views, these skillful experimenters have gone over very nearly the same ground, and their united testimony, concurrent as it is in most cases, gives a certainty to the results obtained which is as fortunate as it is unusual when the field explored is so extensive as the one we are considering. These two men alone could write authoritatively on the subject, and it is, perhaps, fortunate that the first presentation should come from M. Berthelot, who has the usual skill of his nation in exposition and generalization.

In his introduction, Berthelot enunciates the fundamental principles of thermo-chemistry under the three following heads:

Principle of Molecular Work.

I. The quantity of heat evolved is the measure of the sum of the chemical and physical work accomplished in any reaction.

Principle of Conservation of Energy.

II. When a system of bodies—simple or compound—starting from a given condition undergoes either physical or chemical changes, which bring it into a new condition without producing any mechanical effect on external bodies, the amount of heat evolved or absorbed—as the total result of these changes—depends solely on the initial and final states of the system, and is the same, whatever may be the nature or order of the intermediate states.

Principle of Maximum Work.

III. In any chemical reaction between a system of bodies not acted on by external forces, the tendency is toward that condition and those products which will result in the greatest evolution of heat.

The first two of these principles are direct deductions from the mechanical theory of heat; but the third is a generalization, which Berthelot claims as original, and, if so, it is his greatest contribution to this department of the science. In the work before us the two first principles are discussed in the first volume, and this discussion, together with a description of the methods of experimenting and an enumeration of the numerical data thus far obtained, fill nearly 600 large octavo pages; while the discussion of the third principle occupies a second volume which is still larger. We will follow the same order in the few remarks which the limits of a short notice permit.

As the announcement of an almost axiomatic principle of thermo-dynamics, which every investigation of thermo-chemistry necessarily assumes, the first of these general principles has an appropriate place at the opening of a discussion of the subject. In regard to heat, as in regard to other manifestations of energy, the total effect is equal to the sum of all the partial effects. But Berthelot adds to his statement of the Principle of Molecular Work the remark—"This principle furnishes the measure of chemical affinities." When, however, we come to his discussion of this general principle, we are disappointed to find that the whole subject is summarily dismissed without giving the reader any clear conception of the distinction between the two modes of change whose results are so inextricably blended in all chemical processes.

Were we able to distinguish between chemical and physical change, the first principle would undoubtedly give us a measure of what we might then clearly define as chemical affinity or

chemism. Not only, however, is it, at present, impossible to eliminate from our results the effects of physical changes; but, moreover, when we study the details of the chemical processes with which we are most familiar, we are surprised to find to what a large extent the thermal effect depends on the changes in the obviously physical condition which the process involves. For example, in the formation of hydrogen gas from diluted sulphuric acid and zinc, the passing of a solid into a liquid, on the one hand, and the development of a gas from a liquid, on the other, involve physical changes which very largely control the amount of heat developed in the process, and, therefore, also according to the third principle, control the process. Indeed, as is well known, all chemical action ceases as soon as the water becomes saturated with zinc sulphate, although a large excess, both of sulphuric acid and of zinc, may be present. But, after making all allowances for the potency of physical conditions, it would undoubtedly appear from the present standpoint of Chemistry that there must be certain differences of qualities inherent in the atoms, which correspond to differences of chemical affinity and which are important factors in determining chemical changes, and it is certainly legitimate to seek to measure what we may call the relative potential of the atoms when in a state of indefinite expansion. It is obvious, however, from Berthelot's discussion of the subject, that we are, as yet, far from realizing such a result. In fact, the only case in which he claims that we measure directly the heat of chemical action independently of physical changes is in the well-known reaction $H_2+Cl_2=2HCl$, which is attended with the evolution of 22 units of heat for every 36·5 grams of hydrochloric acid gas formed. Since in this case the volume of the aeriform compound is equal to the sum of the volumes of the two elementary gases from which the compound has been formed, and since, moreover, there has been no essential change in the specific heat, we may reasonably infer that the heat evolved results from chemical action only. But, according to the theory which is accepted by the great majority of chemists, this chemical action is by no means so simple as the direct union of two gas volumes would seem to indicate; for, as our symbols show, the process implies the parting of the similar atoms which are united in the molecules, both of hydrogen and of chlorine gases; and, unless we misinterpret a very large number of facts, this separation implies the expenditure of a no inconsiderable amount of mechanical work, and may imply a change of physical condition as well. Berthelot, in common with a school of French chemists, rejects the modern theory based on the assumption of the equal molecular volumes of all substances when in the state of gas, and uses throughout his

work the chemical equivalents of the older chemistry in place of the atomic weights of the new. At the same time he accepts fully the mechanical theory of heat and the conceptions of molecular work which this theory implies. To those who consider that Avogadro's Law, and, therefore, the modern theory of chemistry are direct deductions from the mechanical theory of heat, this course seems inconsistent, and this inconsistency deprives the work of a very considerable degree of simplicity which might otherwise have been secured. The remarkable progress made in organic chemistry during the last twenty years has resulted almost wholly from the circumstance that the investigators have worked back from the elementary substances to the elementary atoms and discussed the various modes in which these atoms might be grouped in the molecules. In the same way in thermo-chemistry we shall find no satisfactory basis until we go back likewise to the atoms and discuss the thermal effects which attend their union or their separation. One generalization we can already make in regard to atomic work with a great degree of certainty;—that the union of atoms is attended with the evolution of heat and the parting of the same atoms in the same associations with an equal absorption of heat:—and it must be remembered that, as defined by modern chemistry, atoms are definite masses of matter, so that in enunciating this general principle we refer to a palpable effect as resulting from a well-defined process, entirely independently of the theoretical views we may have in regard to the nature of the chemical atoms or of the modes by which they are united and grouped together. The general principle just stated explains a great many facts of thermochemistry which are otherwise anomalous and obscure. It moreover gives us the basis for a clear theoretical distinction between a chemical and a physical process, the first consisting in the separation or union of atoms, the last in the separation or drawing together of molecules. It is true that the distinction here drawn is, as yet, theoretical; but the theory involved gives us a basis from which to work, and this is enough for the present. The problem of finding what we have called the thermal potential of the atoms is not more remote than many problems which have been successfully solved in organic synthesis, and it is in this direction, as it seems to us, that we can alone expect to reach a measure of chemical affinity. It may, indeed, be found that the problem cannot be solved and attempts to solve it may lead to results which will modify or supplant our present theories. It may appear that the difference between a chemical and a physical process is one of degree and not of kind; but, whatever the result may be, there can be no doubt that the investigation will lead to larger knowledge and clearer conceptions.

As it seems to us the principle of molecular work should be supplemented by the principle of atomic work, and it is certain that neither clearness of conception nor definiteness of statement has been gained by the obvious attempt to avoid the recognition of the modern theory of chemistry.

We readily accept Berthelot's second fundamental principle of thermo-chemistry when enunciated as above, because it so obviously falls under the general law of conservation of energy; but it is obvious that this principle could not have been assumed prior to its experimental verification, any more than could the principle of the conservation of mass, prior to the experiments of Lavoisier, and as Lavoisier worked out this last great principle with the balance, so Berthelot and Thomsen have demonstrated with the calorimeter the corresponding fundamental principle of thermo-chemistry, which must be regarded as a generalization from the results of their work. Moreover, although in cases of simple direct combination the principle under discussion is almost self-evident, and has been long admitted, yet, before the investigations of Berthelot and Thomsen, no chemist conceived of its application in the very complex and indirect reactions by which the greater part of the thermo-chemical data have been obtained. It must be remembered that very few processes of direct chemical combination fulfill the conditions which an accurate measure of the accompanying thermal change involves, and a vast amount of chemical knowledge and ingenuity has been shown in devising indirect methods by which the results could be reached. The general theory of these indirect methods may be stated thus: We arrange two systems of reactions, both of which begin with the same factors in the same conditions, and end with the same product in the same conditions. In one of these series of reactions there must be no process whose thermal result—if not already known—cannot be measured with the calorimeter. In the other series the chemical combination or decomposition, whose thermal effect we are investigating, enters as an unknown term, the effect of the other chemical changes involved being known or capable of measurement, as in the first series. It follows now, from the principle we are discussing, that if we subtract the sum of the quantities measured in the second series from the sum of those measured in the first series we shall have the value of the unknown quantity. An example will make the method more intelligible.

It is required to determine the heat evolved when aluminum combines with bromine to form Al_2Br_6, and in the following scheme we assume, as is usual in this subject, that the chemical symbols stand for a number of grams corresponding to the atomic weight, and that the amount of heat is expressed in

gram units. Two series of reactions may now be arranged so as to fulfill the conditions we have assumed—

First Series.

K_6+Br_6 (gas) $+Aq=(6KBr+Aq)$	570,000 units.
$Al_2+Cl_6=Al_2Cl_6$	321,800 units.
Al_2Cl_6 dissolved in $(6KBr+Aq)$	152,000 units.
	1,043,800 units.

Second Series.

$K_6+Cl_6+Aq=(6KCl+Aq)$	604,800 units.
$Al_2+Br_6=Al_2Br_6$	x units.
Al_2Br_6 dissolved in $(6KCl+Aq)$	173,800 units.
	778,600 units.

$$x+778{,}600=1{,}043{,}800. \quad x=265{,}200.$$

In studying these two series of reactions it will be evident that we begin in each case with the same amounts of the same elementary substances, namely: K_6, Al_2, Br_6, Cl_6, and that we end with aqueous solutions in the same condition. Hence, the total amount of heat evolved in each of the two series must be the same, and we can at once deduce the value of the only unknown quantity. In this determination the only quantities which had to be measured at the time were the heat of solution of aluminic chloride in an aqueous solution of potassic bromide, on the one hand, and the heat of solution of aluminic bromide in an aqueous solution of potassic chloride, on the other, using, of course, equivalent quantities in each case. The other values given had previously been determined by indirect methods, and it can easily be seen that the investigation displays not only a great command of knowledge but also a great fertility of invention, and yet this is a comparatively simple case.

As deductions from the general principle of the conservation of energy, Berthelot gives a large number of theorems which serve to illustrate the extent and variety of its application to the study of the thermal changes which accompany chemical reactions. We give two as examples:

THEOREM III.—*In two series of reactions starting from different initial conditions, but ending in the same final state, the difference in the quantities of heat evolved is equal to that which would be evolved in passing from one of the initial states to the other.*

This theorem enables us to determine very simply the amount of heat evolved in the formation of the definite hydrates, although it would be very difficult if not impossible to form these substances with a definite composition in the calorimeter. Thus, to determine the heat evolved in the reaction $SO_3+H_2O=H_2SO_4$, we have only to dissolve in one experiment SO_3 and in another H_2SO_4 in a comparatively large amount of

water when the difference in the heat evolved in the two cases will be the quantity required. So, also, the heat of formation of a hydrocarbon may be determined by comparing the heat of combustion of the compound with the heat of combustion of the hydrogen and carbon of which it consists. Thus the heat of combustion of acetylene C_2H_2 (26 grams) has been directly measured and is equal to 321,000 units, while the heat of combustion of C_2 (24 grams) plus the heat of combustion of H_2 (2 grams) only amounts to 257,000 units. Hence, it is evident that in the formation of 26 grams of acetylene 64,000 units are absorbed. Acetylene, indeed, belongs to a class of compounds whose formation is attended with the absorption of heat. This class of compounds which have a special interest in thermo-chemistry are said to be endothermous, while by far the larger class of compounds whose formation is attended with an evolution of heat are said to be exothermous.

THEOREM VI.—*When a compound gives up one of its elements to another body, the heat evolved in the reaction is the difference between the heat of formation of the first compound and that of the resulting product.*

Thus, when an aqueous solution of chlorine is used as an oxidizing agent, for every eighteen grams of water decomposed 9,600 units of heat are evolved, and this amount is the difference between the heat of formation of H_2O and 2HCl. As can easily be seen, the same theroem applies to the problem presented by explosive agents of various kinds and simplifies the solution to a remarkable extent.

These few illustrations will serve to give a general idea of the mode of investigation in this new field of thermo-chemistry, but they are wholly inadequate to show either the extent of the field or the great skill with which it has been cultivated. We must reserve for another number a notice of some very interesting relations which, under his third fundamental principle, Berthelot discusses in the second volume of his great work.

[To be continued.]

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Art. VIII.—*Notice of Julius Thomsen's Thermochemical Investigation of the Molecular Structure of the Hydrocarbon Compounds;** by Josiah P. Cooke.

The value called in thermo-chemistry the heat of formation of a chemical compound is simply the sum of the calorific effects—both positive and negative—of the several processes, by which the compound may be formed from the elementary substances of which it consists. According to a fundamental theorem of thermotics this sum is always the same, by whatever series of processes the compound may be obtained, and may be regarded therefore as representing the amount of heat, which would be evolved by the direct union of the elementary substances, even when the given compound cannot be formed in that way. For convenience of calculation the results are usually stated not for the same weight of each compound, but for its equivalent or molecular weight. Thus when the heat of formation of sulphuric acid (H_2SO_4) is given as $193,000^c$ it is to be understood that 32 grams of solid sulphur, 64 grams of oxygen gas, and 2 grams of hydrogen gas (both gases taken in their ordinary state under the normal conditions of temperature and pressure), when united to form 98 grams of sulphuric acid, evolve sufficient heat to raise the temperature of 193,000 grams of water one degree. It must be noticed that our experiments only prove that in passing from the elementary substances to the ultimate product through the intermediate stages, which the production of sulphuric acid

* Berichte der deutsch. chem. Gesellschaft, xiii, 1880, pp. 1321, 1388, 1806.

involves, a certain amount of heat is lost on balancing the account. The further conclusion that the ultimate loss of heat is precisely the same as it would be if sulphuric acid could be made by the direct union of its elements, is an inference from the general theorem to which we have referred, and which may be stated thus:

Whenever a system of bodies undergoes chemical or physical changes and passes into another condition, whatever may have been the nature or succession of the changes the quantity of heat evolved or absorbed depends solely on the initial and final conditions of the system provided no effect has been produced on the bodies outside.

Hence when the initial and final conditions are the same, the total thermal effect is the same, however different the processes by which the result may be reached. These processes are physical as well as chemical. Thus in the production of sulphuric acid not only has a solid been rendered fluid but also two highly elastic gases have been condensed to the liquid state, changes, which, as is well known, must involve large calorific effects. Were it possible to eliminate the effects of such physical changes, we might hope to determine the amount of heat evolved in the chemical changes alone, and this would give us what we have so long sought, a measure of the forces which determine the union of the elementary atoms. We might then be able to find the amount of heat which would be evolved by the union of 32 grams of isolated sulphur atoms, 64 grams of isolated oxygen atoms, and 2 grams of isolated hydrogen atoms, to form 98 grams of isolated molecules of sulphuric acid. The comparison of such data would give us what we may appropriately call the thermal potentials of the isolated atoms in their several relations, and this would furnish a measure of the various bonds by which the atoms are held in combination, and afford a new and direct method of investigating molecular structures. We should thus obtain a certain criterion for determining the order and the nature of the bonds by which the atoms are united in any molecule. In a recent notice (this Journal, vol. xix, 264, April, 1880), we wrote: "The problem of finding what we have called the thermal potential of the atoms is not more remote than many problems which have been successfully solved in organic synthesis," and we have thus soon the pleasure of calling attention to a partial solution of the problem then stated.

As is well known, in the molecules $C{\equiv}C$; $HC{\equiv}CH$; $H_2C{=}CH_2$; $H_3C{-}CH_3$; $H_4C \mid CH_4$ (the first representing an assumed molecule of carbon in an aeriform condition, and the last representing two molecules of marsh gas) our present theories regard the two carbon atoms as united by four, three, two, one and no bonds respectively; and in the paper we are noticing Thomsen

seeks to determine the thermal value of these several bonds which he represents by the symbols v_4, v_3, v_2 and v_1.

As a starting point for the investigation he has redetermined experimentally the heat of combustion of several of the hydrocarbons, namely Methan CH_4, Ethan C_2H_6, Propan C_3H_8, Propylen C_3H_6, and the values obtained, together with the corresponding values for Ethylene C_2H_4 and Acetylene C_2H_2, previously determined (Pogg. Ann., v. 148, 390), are united in the column under I in the following table. Under column II of the same table we have given the heat of formation of the same hydrocarbons assumed to be produced from amorphous carbon and hydrogen gas. As we already know (from the experiments of Favre and Silbermann and from previous experiments of Thomsen), the heat of combustion both of amorphous carbon and of hydrogen gas, namely,

$$(C, O_2)=96{,}960^c \qquad (H_2, O)=68{,}360^c$$

it is very easy to calculate the values in column II from those in column I; for by a well-known principle of thermo-chemistry the heat of formation of a hydrocarbon is equal to the difference between the heat of combustion of the compound and sum of the similar values for the charcoal and hydrogen gas from which it is assumed to be formed. In the case of CH_4,

$$20{,}150^c=96{,}960^c+2\times68{,}360^c-213{,}530^c.$$

We here assume that the hydrocarbon used in our experiments has the volume it naturally would take under the normal pressure of the air, and hence the values of heat of formation in column II are said to be measured under constant pressure. But as the symbols of the several hydrocarbons represent equal volumes (the same volume as that of a molecule of hydrogen gas represented by H_2) it is evident that the amount of condensation attending the formation of these compounds differs very greatly. Thus if we leave out of view the comparatively insignificant volume of the solid charcoal, it is evident that, while in the formation of CH_4 two volumes are condensed to one, in the formation of C_3H_8 four volumes are condensed to one, and it is evident that if we wish to study the chemical action solely we must eliminate the effect of this mechanical cause of the evolution of heat.

Now it can be calculated from well-known data, that at a mean temperature of 20° C. 580^c are set free for every molecular volume lost by condensation. In the formation of CH_4 from $2H_2$ one molecular volume is lost, and hence by subtracting 580^c from 20,150^c we obtain the amount of heat which would have been evolved had the product occupied the same volume as the factors from which it was formed. In like manner the

other values of column III have been calculated, and we thus obtain what may be called the heat of combination under constant volume.

TABLE I.

	I.	II.	III.
1. CH_4	213,530^c	20,150^c	19,570^c
2. C_2H_6	373,330^c	25,670^c	24,510^c
3. C_3H_8	533,500^c	30,820^c	29,950^c
4. C_2H_4	334,800^c	−4,160^c	−4,740^c
5. C_3H_6	495,200^c	+760^c	−400^c
6. C_2H_2	310,570^c	−48,290^c	−48,290^c

It may be noticed incidentally in connection with this table that the results confirm the previous conclusion of Favre and Silbermann, that the common difference of CH_2 between the members of a series of homologues corresponds in all cases to equal differences in the calorific power of their molecules. Thus from the above table we have

$$C_3H_8 - C_2H_6 = 160,170^c$$
$$C_2H_6 - CH_4 = 159,800^c$$
$$C_3H_6 - C_2H_4 = 160,400^c$$

and it is evident that the difference in question must be very closely 160,000^c.

If, next, we compare the heat of formation under constant volume of all the hydrocarbon molecules which contain two atoms of carbon, we find between these values, also, a manifest relationship, and from this the remarkable conclusions of the paper we are noticing have been deduced.

TABLE II.

	Differences.
$C_2 = -a,$	
	$= 4r$
$C_2 + H_2 = -48,290^c$	
	$43,550 = 3r$
$C_2 + H_4 = -4,740^c$	
	$29,250 = 2r$
$C_2 + H_6 = +24,510^c$	
$2(C+H_4) = C_2 + H_8 = +39,140^c$	$14,630 = r$

Now just as $2CH_4$ is the limit of this series of molecules at one end, C_2 is evidently the limit of the series at the other end, and the symbol C_2 represents the theoretical molecule of carbon in the aeriform state occupying the unit of molecular volume, the two atoms of this molecule united by four bonds. Now if we represent the heat of formation of this molecule by $-a$, it will be seen that the relationship exhibited by the table gives us at once the means of calculating its value. But it is obvious that while the results given in the table are sufficiently accordant to exhibit their relationship, we should obtain quite different values for $-a$ by combining different results, and the nly correct method is to bring all the determinations into the

calculation, combining the several values according to the principle of least squares. This Thomsen has done, and deduced for the most probable values

$$a=106,630^c. \qquad r=14,573.$$

With these values it is now easy to calculate the following table:

TABLE III.

Symbol.	Heat of Formation.	Differences.
C≡C	$-a \quad = -106,630^c$	
HC≡CH	$-a+4r=-48,338^c$	$4r=58,292$
$H_2C=CH_2$	$-a+7r=-4,619^c$	$7r=102,011$
H_3C-CH_3	$-a+9r=24,527^c$	$9r=131,157$
$H_4C \mid CH_4$	$-a+10r=39,100^c$	$10r=145,730$

and by comparing these calculated values with the observed values of table II it will be seen how closely they satisfy the observations. In table III the value $-a$ is the heat of formation of the assumed product C≡C from amorphous charcoal, and is the sum of two quantities, first the amount of heat absorbed in completely disassociating the atoms from the amorphous solid coal, and secondly the amount of heat that must be set free in the union of free carbon atoms in pairs by four bonds. If now we represent the first value by $-2d$ and the second as already proposed by v_4 we can evidently make the equation

$$-a=-2d+v_4=-106,630^c. \qquad (1)$$

If a hydrocarbon is formed from amorphous carbon and hydrogen gas, the process must involve in addition to the disassociation of the atoms of the coal a division of the molecules of hydrogen gas also, and then a union of the hydrogen atoms to the carbon atoms, and perhaps also a union of the carbon atoms by the bonds which remain open one, two or three, as the case may be. Let us represent now by $-hh$ the heat absorbed in the disassociation of the atoms of hydrogen gas, and by ch the heat evolved from the union of the carbon and hydrogen atoms, and by v_3 v_2 v_1 the thermal effect resulting from the union of the carbon atoms by three bonds, two bonds, or a single bond, respectively, and we can at once deduce the following equation which shows the elements of which the heat of formation of acetylene consists:

$$HC{\equiv}CH=(C_2, H_2)=-2d+v_3+2ch-hh. \qquad (2)$$

It will be noticed that the symbols in lower case type are used to represent what we have called the thermal potentials of the atoms.

Assuming, as the facts of organic chemistry undoubtedly justify, that the thermal effect in the union of hydrogen and carbon atoms is always the same, and putting

$$2ch - hh = 2q^{*} \qquad (3)$$

we can readily deduce for the several hydrocarbons we are studying the following equations:

TABLE IV.

For	C≡C	$-a \qquad = -2d + v_4.$
	HC≡CH	$-a + 4r = -2d + v_3 + 2q$
	$H_2C{=}CH_2$	$-a + 7r = -2d + v_2 + 4q$
	$H_3C{-}CH_3$	$-a + 9r = -2d + v_1 + 6q$
	$H_4C \mid CH_4$	$-a + 10r = -2d \ldots\ldots + 8q$

and from the differences between the successive equations of this group we obtain the following simple relations between the quantities we are investigating:

$$v_4 - v_3 = 2q - 4r$$
$$v_3 - v_2 = 2q - 3r$$
$$v_2 - v_1 = 2q - 2r$$
$$v_1 \qquad = 2q - r$$

It will be seen that we have thus made a very near approach to the determination of the thermal value of the several bonds between the carbon atoms, but as in the last group the number of unknown quantities exceeds by one the number of separate equations (it must be remembered that r is known), we must look for some other relation to furnish an additional condition. We can find this, in part at least, in the thermal relations of the oxides of carbon.

The heat of formation of the oxides of carbon from amorphous carbon and oxygen gas, and also the heat of formation of carbonic dioxide from carbonic oxide and oxygen gas are given in the following table:

TABLE V.

	Heat of Formation Under constant pressure.	Under constant volume.
(C, O_2)	96,960^c	96,960^c
$(CO. O)$	68,370^c	68,080^c
(C, O)	28,590^c	28,880^c

The first of these values is the same as that used above, determined by Favre and Silbermann. The second has recently been re-determined by Thomsen. The third is not an experimental value, but deduced by simply subtracting the second from the first. As there is no condensation of gas volume when oxygen gas passes into carbonic dioxide, the heat of formation of carbonic dioxide under constant volume is the same as that under constant pressure. But when carbonic oxide gas unites with oxygen gas to form carbonic dioxide there is a condensation of one half a molecular volume, and hence in this case the value under constant volume is less than that under

* Notice that the quantity q is the result of two processes necessarily simultaneous, the breaking up of the hydrogen molecule and the union of the hydrogen and carbon atoms.

constant pressure by half 580° (page 89). If now we analyze, after the principles applied to the hydrocarbons, the production of the oxides of carbon from amorphous carbon and oxygen gas we can readily deduce the following equations, the meaning of whose terms must be now evident:

$$2(C, O) = -2d - oo + 2co \quad (4)$$

$$(C, O_2) = - d - oo + oco \quad (5)$$

$$(C, O_2) - 2(C, O) = d - 2co + oco = 39{,}200^c. \text{ (Table V).} \quad (6)$$

Here $-oo$ represents the heat absorbed in dividing the molecules of oxygen gas, co the heat evolved in the union of atoms of carbon each with one atom of oxygen and oco the heat evolved in the union of atoms of carbon each with two atoms of oxygen. Could we assume that in the molecule of carbonic dioxide O=C=O the bonds were all of equal value we should necessarily have $oco = 2co$, and then from the last equation we should at once deduce

$$d = 39{,}200^c \quad (7)$$

and this being known the values of v_1 v_2 v_3 and v_4 could at once be definitely calculated from the previous equations. But although the assumption we have made is highly probable, it cannot as yet be proved, and it is possible that

$$2co - oco = x \text{ (some unknown quantity),}$$

and in this case we should have

$$d = 39{,}200^c + x,$$

a value which is independent of all hypothesis.

Returning now to the equations of table IV and taking the numerical values of the left-hand member in each of these equations from table III, we can at once find by simple substitution the following values:

$$q = 14{,}867^c + \frac{x}{4} \quad (8)$$

$$v_4 = C{\equiv}C = -28{,}230^c + 2x \quad (9)$$

$$v_3 = C{\equiv}C = +688^c + \tfrac{3}{2}x \quad (10)$$

$$v_2 = C{=}C = +15{,}033^c + x \quad (11)$$

$$v_1 = C{-}C = +14{,}805^c + \tfrac{1}{2}x \quad (12)$$

Then by subtracting we find the thermal values of the several bonds, which take the following simple forms:

For the first bond	$+ 14{,}805^c + \frac{1}{2}x$	(13)
For the second bond	$+ 228^c + \frac{1}{2}x$	(14)
For the third bond	$- 14{,}345^c + \frac{1}{2}x$	(15)
For the fourth bond	$- 28{,}918^c + \frac{1}{2}x$	(16)

Of course if the probable supposition made above—in regard to the constitution of the molecules of CO_2—is correct, then the terms containing x disappear from all these values.

Again, a very remarkable relation appears when we compare together, as in table VI, the values of r, q, v_1 and v_2.

TABLE VI.

$$r = 14{,}573^{c}$$
$$q = 14{,}687^{c} + \frac{x}{4} = r + \frac{x}{4}$$
$$v_1 = 14{,}805^{c} + \frac{x}{2} = r + \frac{x}{2}$$
$$v_2 = 15{,}033^{c} + x = r + x.$$

It seems highly probable that the numerical term is the same in all these values; and the fact that the same constant frequently appears as a factor in the data of thermo-chemistry renders this conclusion still more probable. Thus we find that the heat of formation of HCl, NO and H_2O (in the condition steam) all as aeriform products under constant pressure is as follows:

$$H_2 + Cl_2 = 44{,}000^{c} = 3 \times 14{,}667^{c}$$
$$N_2 + O_2 = -43{,}150^{c} = 3 \times 14{,}383^{c}$$
$$H_2 + O = 57{,}610^{c} = 4 \times 14{,}402^{c}$$

The constant we have represented by r has evidently then an important significance, and its most probable value is that deduced by the method of least squares from all the observations on the series of hydrocarbons containing two atoms of carbon, as shown by table III. If we take then $r = 14{,}573$ as the true value and $q = r + \frac{x}{4}$, we can easily deduce a second value of d from the data given in the table on page 92. Since $39{,}100^{c} = -2d + 8q$, we have by substituting the value of q, $d = 38{,}742^{c} + x$. From the oxides of carbon we have $d = 39{,}200^{c} + x$. The mean of these values, omitting the last two figures as insignificant, is $d = 38{,}900^{c} + x$.

The following are, now, the most probable values of the chief constants used in this investigation:

TABLE VII.

$d = 38{,}900^{c} + x$	$r = 14{,}570^{c}$
$q = r + \frac{1}{4}x$	$co = 67{,}880^{c}$
$v_1 = r + \frac{1}{2}x$	$v_2 = r + x$
$v_3 = + \frac{3}{2}x$	$v_4 = -2r + 2x$

With these values we can calculate the heat of formation, under constant volume, of a hydrocarbon from amorphous carbon and hydrogen gas, by means of the equation

$$(C_n, H_{2m}) = -nd + 2mq + \Sigma v \qquad (17)$$

in which the Σv is the sum of the calorific effects resulting from the union of the carbon atoms with each other. The results are independent of the unknown quantity x which is eliminated in reducing the equation. Since, as just stated the, unknown quantity x is always eliminated on solving the last

equation we can put $r=q=v_1=v_2=14{,}570$ and $v_3=0$. If also we put $\Sigma v=x_1\ v_1+x_2\ v_2+x_3\ v_3$, ($x_1$, x_2, x_3 representing respectively the number of single, double and treble carbon bonds which occur in the molecule of the hydrocarbon in question), we can write equation (17) in the following more convenient form:

$$(C_n, H_{2m})=-n\times 38{,}900^c+(2m+x_1+x_2)\ 14{,}570^c \qquad (18)$$

This formula may be readily adapted to the various types of hydrocarbons (the paraffines, the olefines, the acetylenes, benzol, etc.), and by its aid we can calculate the heat of formation of different isomers according to their assumed structure, and then on comparing the calculated values with the direct results of experiment we may hope to obtain a new test of our theories of molecular structure.

In the series of paraffines the carbon atoms are all linked by single bonds, and no isomerism resulting from different relations of the carbon bonds is possible. Of course isomerism can result from differences in the grouping of the carbon atoms, but of this our thermo-chemical theory takes, as yet, no account. The general formula of a paraffine is $C_n\ H_{2n+2}$ and the number of single carbon bonds is $n-1$. We have then $2m=2n+2$; $x_1=n-1$; $x_2=0$. Making these substitutions in (18) we have

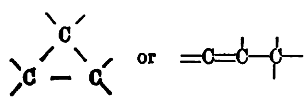
$$(C_n, H_{2n+2})=n\times 4810^c+14570^c \qquad (19)$$

and the calculated values of the heat of formation under constant volume for the first three members of the series is as follows. The observed values in the parallel column shows as close accordance as could be expected.

TABLE VIII.

	Calculated.	Observed.
CH_4	19,380°	19,570°
C_2H_6	24,190°	24,510°
C_3H_8	29,000°	39,950°

In the olefines, however, isomerism resulting from different relations of the carbon bonds is possible; thus in the case of C_3H_6 we may have



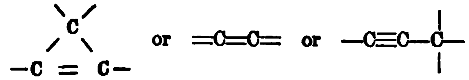
The general formula of an olefine being C_nH_{2n}, we have in the first case n single carbon bonds, and in the second case $n-2$ single bonds together with one double bond. Making the obvious substitutions in equation (18), we have for the heat of formation under constant volume

(1) $(C_n, H_{2n}) = n\times 4810^c$

(2) $(C_n, H_{2n}) = n\times 4810^c - 14{,}570^c$

For propylene $n = 3$, and the calculated values are $+14{,}430^c$ or -150^c. According to Thomsen's experiments the heat of formation of propylene prepared from isopropyliodide is -400^c, which would indicate that the generally received opinion in regard to the structure of this molecule is correct.

With the acetylenes we may have three distinct types of structure depending on the distribution of the carbon bonds. Thus for C_3H_4 either



The general symbol for an acetylene being $C_n\ H_{2n-2}$ we have in isomers of the first type $n-1$ single with one double bond; in isomers of second type $n-3$ single with two double bonds, and in isomers of the third type $n-2$ single with one treble bond. Making the substitutions as before, we obtain the following equations:

$$(1)\quad (C_n, H_{2n} - 2) = n \,.\, 4810^c - 29140^c$$
$$(2)\quad (C_n, H_{2n} - 2) = n \,.\, 4810^c - 43710^c$$
$$(3)\quad (C_n, H_{2n} - 2) = n \,.\, 4810^c - 58280^c$$

and for allylene the three values are

$$-14710^c \qquad -29283^c \qquad -43856^c$$

A determination of the heat of combustion of allylene was made by Berthelot, and since the heat of formation under constant volume deduced from his experiment is $-38{,}320^c$, it is probable that the last of the three symbols above represents the ordinary type of structure and this again is in accordance with the generally received opinion. The discrepancy between theory and observation, however, is quite large, and Thomsen intends to make further experiments on this substance.

One feature of this investigation of Thomsen, which might be overlooked unless attention was called to it, may be appropriately noticed in this connection. Omitting the unknown quantity x, which indeed is probably zero, we have for the values of the carbon bonds,

$$v_1 = r \qquad v_2 = r \qquad v_3 = 0 \qquad v_4 = -2r$$

and $r = 14\,570^c$. Hence it follows that the same energy results whether two carbon atoms unite by one or by two bonds, and that when they unite by three bonds no energy whatever is set free. At first sight this result seems strange, for we should naturally expect that the larger the number of bonds of union, the greater would be the force required to separate these atoms and hence the greater the manifestation of energy when these atoms united. On the contrary this investigation shows that if two carbon atoms are united by two bonds it requires no

energy to break one of the bonds if the other is left unimpaired, although it requires an energy measured by 14,770° to break the last. While if the atoms are united by three bonds there is as strong a tendency to break away at the first bond as there is to hold together at the last bond.

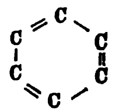
Strange, however, as these results may appear, they harmonize with the known chemical relations of the paraffines, olefines and acetylenes. The stability of a chemical compound is to a certain extent proportional to the amount of energy set free in its production; since in order to decompose it the same amount of energy must be expended. In the paraffines, where all the carbon atoms are united by single bonds, and all the other bonds closed by hydrogen atoms, the molecules can not be decomposed unless one at least of the bonds is broken, and each break, whether between *cc* or *hc*, implies an expenditure of energy represented by 14,570°. Here then is the explanation of the great stability of this class of hydrocarbons.

Passing next to the olefines we find a very different condition. In every molecule of these bodies two of the carbon atoms are united by a double bond, and one of the two can be broken without the expenditure of energy, so that atoms of chlorine or bromine have no work to do in order to unite at these points except to free themselves from their previous association. Hence arises the most familiar and characteristic chemical property of these substances.

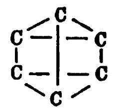
Lastly, in the acetylenes the same tendency is still more strongly marked; for in the molecules of these bodies two of the carbon atoms are united by a treble bond, and the parting of either one or of two of these bonds is attended with a development of energy which is added to that resulting from the normal attraction of the carbon atoms for other radicals.

But the molecular structure of none of the more complex hydrocarbons has been so fully studied as that of benzol (C_6H_6), and we therefore have naturally waited with great interest for the results of the application of the new method of investigation to this compound. In the last number of the Berichte der deutsch. chem. Gesellschaft (Oct. 25, 1880), the expected results are published. In the benzol molecule, six only of the twenty-four bonds, which belong to six carbon atoms, are closed by hydrogen atoms leaving eighteen bonds to unite with each other, or nine connecting bonds as they are usually represented. Now we can conceive of a number of different ways in which these bonds may be distributed; but there are only two schemes which will satisfy the well-known facts in regard to the three types of isomeric derivatives of benzol. These schemes are that of Kékulé represented in fig. 1, and that of Ladenburg in fig. 2.

1.



2.



In the first scheme there are three single and three double bonds; in the second scheme nine single bonds. Making now the obvious substitutions in equation (18), we obtain for the heat of formation under constant volumes either

$$-60,360^c \text{ or } -16,650^c,$$

and for the heat of formation under constant pressure

$$-59,200^c \text{ or } -15,490^c.$$

We can now easily calculate, by the method already described, the heat of combustion of benzol vapor and we shall obtain

$$846,040^c \text{ or } 802,330^c.$$

Finally, Thomsen has re-determined with great care the same value and finds as the mean of five experiments that the heat of combustion of the molecular weight of benzol (72 gr.) is 805,800^c. Hence he concludes:

"The six carbon atoms of benzol are united to each other by nine single bonds, and the previous assumption of a structure of benzol with three single and three double bonds is not supported by experiment."

Thomsen endeavors to prepare the way for the reception of this conclusion by emphasizing the statement that: "*The great resisting power of benzol militates against the presence of multiple bonds.*" But although it is true that chlorine or bromine act on benzol far more feebly than on ethylene or acetylene, nevertheless, under no great stress, benzol does yield addition products, and there can be no question that the original scheme of Kékulé harmonizes more chemical facts than the modification of this scheme proposed by Ladenburg. The new evidence is very important, but until its bearing has been more fully investigated it can not be regarded as conclusive. Indeed the interest of this investigation depends not so much on its results as on its method. It is a bold push beyond the beaten tracks of science, and although the first results of the venture must be accepted with caution, the skill displayed calls forth our admiration and the importance of the methods employed justifies this extended notice.

Zürich, were used for the preparation of these products. The needles, in which the peculiar odor seemed to be most abundant, were stripped from the twigs and distilled with water in a large copper retort in a current of steam from a boiler. The distillate was agitated with ether and the ether distilled off. The early portions of the distillate gave only a solid residue, the next gave a mixture of solid and liquid, and the last portions only an oil. The solid substance was with some difficulty obtained crystallized. It is very soluble in alcohol, ether, benzene and chloroform. In ligroin (petroleum naphtha) it is less so. In glacial acetic acid, it is soluble only on heating. By covering its solution in this acid with a layer of water, the gradual solution of the acid caused a deposition of this body in small crystal plates, fusing at 105°. They are white, have a bluish fluorescence, and possess the penetrating aromatic odor of Sequoia in a high degree. When thus concentrated, it recalls the odor of peppermint. Its boiling point was between 290° and 300°, and it gave on analysis C 93·55, H 6·09, corresponding to the formula $C_{13}H_{10}$. Its vapor density by v. Meyer's method, was 81·7; the above formula requires 83. This empirical formula is that of fluorene; but its fusing point and general properties distinguish it from this body. The authors give it the name *sequoiene* and are engaged in its study. The liquid distillates gave: (1) a colorless oil boiling at 155°; (2) a slightly yellow oil, fusing point 190°–200°; (3) a yellow oil fusing at 240°; and (4) a solid body fusing at 290°–300° evidently sequoiene.—*Ber. Berl. Chem. Ges.*, xiii, 1656, Sept., 1880.

G. F. B.

5. *On Bäyer's Synthesis of Indigotin.*—ROSENSTIEHL has given a summary of the processes discovered and patented by Bäyer for the synthesis of indigotin. The point of departure in both of these is cinnamic or phenyl-acrylic acid, $C_6H_5(C_3H_3O_2)$. Nitric acid produces from this nitrocinnamic acid, the nitryl occupying the ortho position in that form of the acid which yields indigotin. The orthonitrocinnamic acid is transformed by known processes either into orthonitrophenylpropiolic or into orthonitrophenyloxyacrylic acid, according to the process to be followed subsequently. To transform it into orthonitrophenylpropiolic acid, the orthonitrocinnamic acid is brominated, giving $C_6H_4(NO_2)(C_3H_3Br_2O_2)$. By the action of alkali in boiling alcoholic solution $(HBr)_2$ is removed, leaving $C_6H_4(NO_2)(C_3HO_2)$ orthonitrophenylpropiolic acid. To produce orthonitrophenyloxyacrylic acid, the orthonitrocinnamic acid is treated with hypochlorous acid, which by addition gives orthonitrophenylchlorolactic acid, $C_6H_4(NO_2)(C_3H_4ClO_3)$. This, treated with boiling alkali in alcohol, gives orthonitrophenylacrylic acid $C_6H_4(NO_2)(C_3H_3O_3)$. By the action of heat alone orthonitrophenylacrylic acid is converted into indigotin, thus:

$$C_9H_7NO_5 = C_8H_5NO + CO_2 + H_2O + O.$$

The reaction takes place at 110° C. The mass swells, its color gradually darkens, and, treated with alcohol, it leaves a residue

of indigotin. The yield is small, however, owing to the formation of secondary products. With orthonitrophenylpropiolic acid however, the united action of an alkali and of a deoxidizing body is required, the reaction proceeding regularly:

$$C_9H_5NO_4+H_2=C_8H_5NO+CO_2+H_2O.$$

Bäyer recommends the use of a mixture of glucose and an alkali carbonate. The transformation takes place at 110° C. and the indigotin separates in the crystalline form. Hence Bäyer prefers the second process. But it has a still greater advantage, since the above reaction may be effected directly upon the cloth. The fiber is printed with a mixture of the orthonitrophenylpropiolic acid, glucose and the alkali carbonate and is then exposed to superheated steam. The indigo blue is developed directly upon the fiber permanently. This fact will give the artificial indigo a great advantage over the natural product. The possibility of producing other indigotines by effecting substitutions in the phenyl group which it contains, promises important results.—*Ann. Chim. Phys.*, V, xxi, 286, Oct., 1880. G. F. B.

6. *On Isopropylene-neurine.*—MORLEY has prepared, in the laboratory of Ad. Wurtz, a neurine containing oxyisopropyl in place of the oxethyl in normal neurine. By the action of 20 grams isopropylene-chlorhydrin upon 37 grams of a 33 per cent solution of trimethylamine for several hours on the water bath, a neutral liquid resulted which gave a platinum salt of the composition $C_{12}H_{32}N_2O_2PtCl_6$. The propylene-neurine chloride crystallizes in colorless transparent crystals, very deliquescent, and which turn brown in the air.—*Ber. Berl. Chem. Ges.*, xiii, 1805, Oct., 1880. G. F. B.

7. *Notice of the investigation of* Dr. J. W. BRUHL *on the Relations between the Molecular Structure of Organic Compounds and their Refractive Power.* (Liebig's Annalen, cxcix, 139 and cciii, 1.)—The study of the relations between the physical properties of chemical compounds and their molecular structure has opened a new field to the science of chemistry. A remarkable investigation of Thomsen into some of the thermal relations of molecular structure, we shall notice in another number of this Journal. We now call attention to an attempt to study the molecular structure of bodies by optical means. Unfortunately the results of the two investigations do not wholly harmonize with one another; yet in both cases the new method of investigation is the chief point of interest, and we have every reason to hope that by carefully comparing the different methods of solving the same problem the truth may ultimately be reached.

If we denote by μ the index of refraction of a body the excess of this index over unity or $(\mu-1)$ represents what has been called the refracting power of a body, and since the refracting power increases in general with the density (δ) we obtain by dividing the refracting power by the density a quantity $\left(\frac{\mu-1}{\delta}\right)$ which is, essentially, independent of mere changes of physical condition, and depends on

the chemical relations of the substances. This quantity has been called the specific refracting power, and if we now multiply by the molecular weight of the substance we have in $M\left(\frac{\mu-1}{\delta}\right)$ the specific refracting power of the molecule, or as it has also been called the refractive equivalent of the substance. In 1864 (Pogg. Ann., cxxiii, 595) Landolt showed that a difference of one atom of carbon, hydrogen or oxygen, between two organic compounds corresponded to a constant difference for each elementary substance in the specific refracting power of the molecule, and having thus fixed what he called the refractive power of each atom he made the generalization that the refractive power of the molecule was simply the sum of the refractive powers of its constituent atoms. For example:

TABLE I.

		$M\left(\frac{\mu-1}{a}\right)$	Diff.
	Differing in composition by C_1.		
Methyl alcohol	CH_4O	13·17	5·41
Aldehyde	C_2H_4O	18·58	
	Differing in composition by H_2.		
Aldehyde	C_2H_4O	18·58	2·12
Ethyl alcohol	C_2H_6O	20·70	
	Differing in composition by O_1.		
Aldehyde	C_2H_4O	18·58	2·53
Acetic acid	$C_2H_4O_2$	21·11	

The differences show the refractive power of one atom of carbon, one atom of oxygen and two atoms of hydrogen and the following values are in each case, the mean of a very large number of comparisons similar to those just given.

TABLE II.

	r_a	r_A
C	5·0	4·86
H	1·3	1·29
O	3·0	2·90

Of course these values are based on the determination of the index of refraction, and the density of each of the substances thus compared. The observations of density were readily reduced to standard conditions which might be arbitrarily selected, but in consequence of the very unequal and irregular dispersive power of the different substances compared it was by no means a matter of indifference which of the lines of the spectrum was selected for the index of refraction. In his own experiments Bruhl determined the index of refraction for the sodium line D and also for the three bright hydrogen lines, and by means of these data he calculated according to Cauchy's formula the index of refraction corresponding to a wave length of indefinite length, and from these calculated indices the values r_A are derived. Data thus reduced are regarded by Bruhl as furnishing the more correct

basis for all comparisons of molecular refractive powers, but the results are nearly as satisfactory when deduced from the indices observed with the red light of the hydrogen spectrum. The values r_a were thus obtained.

If now we compare the molecular refractive powers calculated from the atomic composition (R_a) with those deduced from direct observations on the densities and indices of refraction of the compounds—$M\left(\frac{\mu_a - 1}{\delta}\right)$—we shall find that in the case of a large number of organic products the generalization of Landolt is very closely confirmed, thus:

TABLE III.

		$M\left(\frac{\mu_a-1}{\delta}\right)$	R_a	Diff.
Propylalcohol	C_3H_8O	28·6	28·4	+0·2
Propylaldehyde	C_3H_6O	26·0	25·8	+0.2
Propylethyl ether	$C_5H_{12}O$	43·8	43·6	+0.2
Propylacetate	$C_5H_{10}O_2$	44·0	44·0	0·0
Propylchloride	C_3H_7Cl	34·1	33·9	+0·2
Isobutyric acid	$C_4H_8O_2$	36·3	36·4	−0·1
Hexan	C_6H_{14}	48·6	48·2	+0·4
Tri-ethylamine	$C_6H_{15}N$	55·3	55·3	0·0

If then the molecular refractive power is simply the sum of the atomic refractive powers it must be the same for all isomeric bodies and therefore independent of their molecular structure, and so Landolt thought. In 1870, however, it was shown by Gladstone (London Chem. Soc. Jour., viii, 147) that there were many organic compounds, especially those belonging to the aromatic family, whose molecular refractive powers differed from the values calculated by Landolt's formula so widely, that the discrepancies could not possibly be referred to errors of observation. The residuals thus observed although not satisfactorily explained by Gladstone form the starting point in the investigation of Bruhl, who traces the effect to the mode of linking of the multivalent atoms in the molecule. He concludes in general that, while the univalent atoms of hydrogen, chlorine, bromine and iodine, have an invariable refracting power, the refracting power of multivalent atoms changes when they unite with each other by more than one bond. The values given in table II only hold rigorously, when no two atoms are united by more than a single bond, and the close agreement shown in table III depends on the circumstance that the molecules of all the substances therein named, however variable their structure in other respects, have this one feature in common. Hence all isomeric bodies have the same molecular refractive power, provided the differences of molecular structure do not extend to the relation we have named; and the discrepancies observed by Gladstone arose from the circumstance that in the molecules of the bodies he chiefly studied two or more of the carbon atoms were linked by double or treble bonds.

By comparing the molecular refractive powers of bodies containing doubly or trebly linked multivalent atoms, after the

method illustrated by table I, Bruhl has determined the effect of the double and treble links in the case of carbon, and of the double links in the case of oxygen, on the atomic refracting power, and has thus obtained the data for the following table. In this table C′ C″ C‴ indicate carbon atoms singly, doubly and trebly linked with each other, and O″ an atom of oxygen doubly linked to an atom of carbon, and in order that the values given may be used in calculating the molecular refractive power of organic compounds it must be further noticed that the value for the group $-\overset{\overset{O}{\|}}{C}-$ is $5+3{\cdot}4 = 8{\cdot}4$ and that for the group $-\overset{|}{C}=\overset{|}{C}-$ is $2 \times 6{\cdot}15 = 12{\cdot}3$.

TABLE IV.

	r_a	r_A
C′	5·00	4·86
C″	6·15	5·86
C‴	5·95	5·76
O′	2·80	2·71
O″	3·40	3·29
H	1·30	1·29
Cl	9·80	9·53
Br	15·30	14·75
T	24·90	23·55
N′	5·80	5·35

With these data it is now easy to calculate the molecular refractive powers of the greater number of organic compounds, not only the parafines and their derivatives in which the carbon atoms are usually singly linked, but also the olefines, the acetylenes and the aromatic bodies, in which the complexity of the structure is increased by double or treble links. In the original papers such results are compared with the molecular refractive powers calculated by Landolt's formula from the index of refraction and density, measured with every refinement, and with materials of undoubted purity. In almost all cases the agreement is exceedingly close especially when the observations are reduced by Cauchy's formula so as to eliminate the effect of the irregular dispersive powers of the substances compared. We have not however room to reprint the numerous tables or to describe the details of the investigation which involve many incidental points of great interest. It must be sufficient to say that the papers show that the work has been done with all the care and refinements of which the methods used are capable, and limit ourselves to a description of one only of the important conclusions to which the investigations points.

It is obvious that, when a question in regard to molecular structure turns on the existence or absence of multiple bonds, the calculated molecular refractive power will not be the same in the two cases and then the index of refraction and the density of the substance may give us the means of testing our hypothesis. As is well known there has been a question in regard to the molecu-

lar structure of benzol, C_6H_6. According to the well known theory of Kekulé the six carbon atoms form a ring and are united by three single and three double bonds; but according to the theory of Ladenburg, the bonds in this structure are all single, each carbon atom being united with two of the other carbon atoms of the ring. The principles developed by Bruhl give him a new test of the theories in question since the molecular refractive power should be six units higher with the structure of Kekulé than with that of Ladenburg, and as the value deduced from the observed index of refraction and density of benzol gives a result which very closely agrees with the larger of the two values, Bruhl concludes that the generally received theory of Kekulé is "the only one which harmonizes with the physical as well as the chemical relations of the aromatic compounds."

J. P. COOKE.

8. *Chemical Energy and Electromotive force of different galvanic elements.*—THOMSEN reviews his earlier work upon this subject and makes a new and careful determination of the chemical energy and the electromotive force of a Daniells cell. According to his later measurements, the total devlopment of heat by galvanic means in all parts of the Daniells element amounts to 50292 units of heat during the time in which one molecule of copper sulphate ($CuSO_4$) is reduced. A calculation of the value of the energy of the chemical processes in the cell gives 50130 units. The difference between 50292 and 50130 is so small that Thomsen concludes that the total chemical energy of a Daniells cell is converted into electricity and the development of heat in the circuit is the equivalent of the chemical energy developed by the cell. Other forms of cells are then investigated from this point of view and the same conclusion is reached in the case of zinc-cadmium elements and chloride of silver elements, or in general wherever the metallic surface of the negative electrode is not changed by the electrolytic process.—*Ann. der Physik und Chemie*, No. 10, 1880, p. 246.

J. T.

9. *Spectra of the compound of Carbon with Hydrogen and Nitrogen.*—Professors LIVEING and DEWAR used in their experiments a DeMeritens dynamo-electric machine which produced the voltaic arc in the different gases they experimented upon. It was found that the indigo, violet and ultra violet bands characteristic of the flame of cyanogen are conspicous in the arc taken in an atmosphere of nitrogen, air, nitric oxide or ammonia, and disappear very nearly in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine. These bands are seen in the flame of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The authors therefore conclude that they belong to cyanogen, and support this conclusion by reference to various facts. Their experiments on the spectrum of carbon are at variance with those of Lockyer on the same subject. They state that the evidence that carbon uncombined can take the state of vapor at the tempera-

SCIENTIFIC CULTURE.

By JOSIAH P. COOKE, Jr.,
PROFESSOR OF CHEMISTRY AND MINERALOGY IN HARVARD COLLEGE.

YOU have come together this morning to begin various elementary courses of instruction in chemistry and mineralogy. As I have been informed, most of you are teachers by profession, and your chief object is to become acquainted with the experimental methods of teaching physical science, and to gain the advantages in your study which the large apparatus of this university is capable of affording. In all this I hope you will not be disappointed. You, as teachers, know perfectly well that success must depend, first of all, on your own efforts; but, since the methods of studying Nature are so different from those with which you are familiar in literary studies, I feel that the best service I can render, in this introductory address, is to state, as clearly as I can, the great objects which should be kept in view in the courses on which you are now entering.

By your very attendance on these courses you have given the strongest evidence of your appreciation of the value of chemical studies as a part of the system of education, and let me say, in the first place, that you have not overvalued their importance. The elementary principles and more conspicuous facts of chemistry are so intimately associated with the experience of every-day life, and find such important applications in the useful arts, that no man at the present day can be regarded as educated who is ignorant of them. Not to know why the fire burns, or how the sulphur-trade affects the industries of the world, will be regarded, by the generation of men among whom your pupils will have to win their places in society, as a greater mark of ignorance than a false quantity in Latin prosody or a solecism in grammar. Moreover, I need not tell you that physical science has become a great power in the world. Indeed, after religion, it is the

[1] An Address delivered July 7, 1875, at the opening of the Summer Courses of Instruction in Chemistry, at Harvard University.

greatest power of our modern civilization. Consider how much it has accomplished during the last century toward increasing the comforts and enlarging the intellectual vision of mankind. The railroad, the steamship, the electric telegraph, photography, gas-lights, petroleum-oils, coal-tar colors, chlorine-bleaching, anæsthesia, are a few of its recent material gifts to the world; and not only has it made one pair of hands to do the work of twenty, but it has so improved and facilitated the old industries that what were luxuries to the fathers of our republic have become necessities to our generation. And when, passing from these material fruits, you consider the purely intellectual triumphs of physical science, such as those which have been gained with the telescope, the microscope, and the spectroscope, you cannot wonder at the esteem in which these branches of study are held in this practical age of the world.

Now, these immense results have been gained by the application to the study of Nature of a method which was so admirably described by Lord Bacon in his "Novum Organon," and which is now generally called the experimental method. What we observe in Nature is an orderly succession of phenomena. The ancients speculated about these phenomena as well as ourselves, but they contented themselves with speculations, animating Nature with the products of their wild fancies. Their great master, Aristotle, has never been excelled in the art of dialectics; but his method of logic applied to the external world was of very necessity an utter failure. It is frequently said, in defense of the exclusive study of the records of ancient learning, that they are the products of thinking, loving, and hating men, like ourselves, and it is claimed that the study of science can never rise to the same nobility because it deals only with *lifeless* matter. But this is a mere play on words, a repetition of the error of the old schoolmen. Physical science is noble because it does deal with thought, and with the very noblest of all thought. Nature at once manifests and conceals an Infinite Presence: Her methods and orderly successions are the manifestations of Omnipotent Will; Her contrivances and laws the embodiment of Omniscient Thought. The disciples of Aristotle so signally failed simply because they could see in Nature only a reflection of their idle fancies. The followers of Bacon have so gloriously succeeded because they approached Nature as humble students, and, having first learned how to question Her, have been content to be taught and not sought to teach. The ancient logic never relieved a moment of pain, or lifted an ounce of the burden of human misery. The modern logic has made a very large share of material comfort the common heritage of all civilized men.

In what, then, does this Baconian system consist? Simply in these elements: 1. Careful observation of the conditions under which a given phenomenon occurs; 2. The varying of these conditions by experiments, and observing the effects produced by the variation. We

thus find that some of the conditions are merely accidental circumstances, having no necessary connection with the phenomenon, while others are its invariable antecedent. Having now discovered the true relations of the phenomenon we are studying, a happy guess, suggested probably by analogy, furnishes us with a clew to the real causes on which it depends. We next test our guess by further experiments. If our hypothesis is true, this or that must follow; and, if in all points the theory holds, we have discovered the law of which we are in search. If, however, these necessary inferences are not realized, then we must abandon our hypothesis, make another guess, and test that in its turn. Let me illustrate by two well-known examples:

The, of old, universally accepted principle that all living organisms are propagated by seeds or germs (*omnia ex ovo*) has been seriously questioned by a modern school of naturalists. Various observers have maintained that there were conditions under which the lower forms of organic life were developed independently of all such accessories, but other, and equally competent, naturalists who have attempted to investigate the subject, have obtained conflicting results. Thus it was observed that certain low forms of life were quite constantly developed in beef-juice that had been carefully prepared and hermetically sealed in glass flasks, even after these flasks had been exposed for a long time to the temperature of boiling water. "Here," proclaims the new school, "is unmistakable evidence of spontaneous generation; for, if past experience is any guide, all germs must have been killed by the boiling water." "No," answer the more cautious naturalists, "you have not yet proved your point. You have no right to assume that all germs are killed at this temperature." The experiments, therefore, were repeated under various conditions and at different temperatures, but with unsatisfactory results, until Pasteur, a distinguished French physicist, devised a very simple mode of testing the question. He reasoned thus: "If, as is generally believed, the presence of invisible spores in the air is an essential condition of the development of these lower growths, then their production must bear some proportion to the abundance of these spores. Near the habitations of animals and plants, where the spores are known to be in abundance, the development would be naturally at a maximum, and we should expect that the growth would diminish in proportion as the microscope indicated that the spores diminished in the atmosphere." Accordingly, Pasteur selected a region in the Jura Mountains suitable for his purpose, and repeated the well-known experiment with beef-juice, first at the inn of a town at the foot of the mountains, and then at various elevations up to the bare rocks which covered the top of the ridge, a height of some 8,000 feet. At each point he sealed up beef-juice in a large number of flasks and watched the result. He found that while in the town the animalcules were developed in almost all the flasks, they appeared

only in two or three out of a hundred cases where the flasks had been sealed at the top of the mountain, and to a proportionate extent in those sealed at the intermediate elevations. What, now, did these experiments prove? Simply this, that the development of these organic forms was in direct proportion to the number of germs in the air. It did not settle the question of spontaneous generation, but it showed that false conclusions had been deduced from the experiments which had been cited to prove it.

A still more striking illustration of the same method of questioning Nature is to be found in the investigation of Sir Humphry Davy on the composition of water. The voltaic battery which works our telegraphs was invented by Volta in 1800; and later, during the same year, it was discovered in London, by Nicholson and Carlisle, that this remarkable instrument had the power of decomposing water. These physicists at once recognized that the chief products of the action of the battery on water were hydrogen and oxygen gases, thus confirming the results of Cavendish, who in 1781 had obtained water by combining these elementary substances; oxygen having been previously discovered in 1775, and hydrogen at least as early as 1766. It was, however, very soon also observed that there were always formed by the action of the battery on water, besides these aëriform products, an alkali and an acid, the alkali collecting around the negative pole and the acid around the positive pole of the electrical combination. In regard to the nature of this acid and alkali there was the greatest difference of opinion among the early experimenters on this subject. Cruickshanks supposed that the acid was nitrous acid, and the alkali ammonia. Desormes, a French chemist, attempted to prove that the acid was muriatic acid; while Brugnatelli asserted that a new and peculiar acid was formed, which he called the electric acid.

It was in this state of the question that Sir Humphry Davy began his investigation. From the analogies of chemical science, as well as from the previous experiments of Cavendish and Lavoisier, he was persuaded that water consisted solely of oxygen and hydrogen gases, and that the acid and alkali were merely adventitious products. This opinion was undoubtedly well-founded; but, great disciple of Bacon as he was, Davy felt that his opinion was worth nothing unless substantiated by experimental evidence, and accordingly he set himself to work to obtain the required proof.

In Davy's first experiments the two glass tubes which he used to contain the water were connected together by an animal membrane, and he found, on immersing the poles of his battery in their respective tubes, that, besides the now well-known gases, there were really formed muriatic acid in one tube and a fixed alkali in the other. Davy at once, however, suspected that the acid and alkali came from common salt contained in the animal membrane, and he therefore rejected this material and connected the glass tubes by carefully-washed cotton

fibre: when, on submitting the water as before to the action of the voltaic current, and continuing the experiment through a great length of time, no *muriatic* acid appeared; but he still found that the water in the one tube was strongly alkaline, and in the other strongly acid, although the acid was, chiefly at least, nitrous acid. A part of the acid evidently came from the animal membrane, but not the whole, and the source of the alkali was as obscure as before. Davy then made another guess. He knew that alkali was used in the manufacture of glass; and it occurred to him that the glass of the tubes, decomposed by the electric current, might be the origin of the alkali in his experiments. He therefore substituted for the glass tubes cups of agate, which contains no alkali, and repeated the experiment, but still the troublesome acid and alkali appeared. Nevertheless, he said, it is possible that these products may be derived from some impurities existing in the agate cups, or adhering to them; and so, in order to make his experiments as refined as possible, he rejected the agate vessels and procured two conical cups of pure gold, but on repeating the experiments the acid and alkali again appeared.

And now let me ask who is there of us who would not have concluded at this stage of the inquiry that the acid and alkali were essential products of the decomposition of water? But not so with Davy. He knew perfectly well that all the circumstances of his experiments had not been tested, and until this had been done he had no right to draw such a conclusion. He next turned to the water he was using. It was distilled water, which he supposed to be pure, but still, he said, it is possible that the impurities of the spring-water may be carried over to a slight extent by the steam in the process of distillation, and may therefore exist in my distilled water to a sufficient amount to have caused the difficulty. Accordingly he evaporated a quart of this water in a silver dish, and obtained seven-tenths of a grain of dry residue. He then added this residue to the small amount of water in the gold cones and again repeated the experiment. The proportion of alkali and acid was sensibly increased.

You think he has found at last the source of the acid and alkali in the impurities of the water. So thought Davy, but he was too faithful a disciple of Bacon to leave this legitimate inference unverified. Accordingly he repeatedly distilled the water from a silver alembic until it left absolutely no residue on evaporation, and then with water, which he knew to be pure, and contained in vessels of gold from which he knew it could acquire no taint, he still again repeated the already well-tried experiment. He dipped his test-paper into the vessel connected with the positive pole, and the water was still decidedly acid. He dipped the paper into the vessel connected with the negative pole, and the water was still alkaline.

You might well think that Davy would have been discouraged here. But not in the least. The path to the great truths which

Nature hides often leads through a far denser and a more bewildering forest than this; but then there is not infrequently a *blaze* on the trees which points out the way, although it may require a sharp eye in a clear head to see the marks. And Davy was well enough trained to observe a circumstance which showed that he was now on the right path and heading straight for the goal. On examining the alkali formed in this last experiment, he found that it was not, as before, a fixed alkali, soda or potash, but the volatile alkali ammonia. Evidently the fixed alkali came from the impurities of the water, and when, on repeating the experiment with pure water in agate cups or glass tubes, the same results followed, he felt assured that so much at least had been established. There was still, however, the production of the volatile alkali and of nitrous acid to be accounted for. As these contain only the elements of air and water, Davy thought that possibly they might be formed by the combination of hydrogen at the one pole and of oxygen at the other with the nitrogen of the air, which was necessarily dissolved in the water. In order, therefore, to eliminate the effect of the air, he again repeated the experiment under the receiver of an air-pump from which the atmosphere had been exhausted, but still the acid and alkali appeared in the two cups.

Davy, however, was not discouraged by this, for the *blazes* on the trees were becoming more numerous, and he now felt sure that he was fast approaching the end. He observed that the quantity of acid and alkali had been greatly diminished by exhausting the air, and this was all that could be expected, for, as Davy knew perfectly well, the best air-pumps do not remove all the air. He therefore for the last experiment not only exhausted the air, but replaced it with pure hydrogen, and then exhausted the hydrogen and refilled the receiver with the same gas several times in succession, until he was perfectly sure that the last traces of air had been as it were washed out. In this atmosphere of pure hydrogen he allowed the battery to act on the water, and not until the end of twenty-four hours did he disconnect the apparatus. He then dips his test-paper into the water connected with the positive pole, and there is no trace of acid; he dips it into the water at the negative pole, and there is no alkali; and you may judge with what satisfaction he withdraws those slips of test-paper, whose unaltered surfaces showed that he had been guided at last to the truth, and that his perseverance had been rewarded.

The fame of Sir Humphry Davy rests on his discovery of the metals of the alkalies and earths which first revealed the wonderful truth that the crust of our globe consists of metallic cinders; but none of these brilliant results show so great scientific merit or such eminent power of investigating Nature as the experiments which I have just detailed. I have not, however, described them here for the purpose of glorifying that renowned man. His honored memory needs no such office at my hands. My only object was to show you what is

meant by the Baconian method of science, and to give some idea of the nature of that modern logic which within the last fifty years has produced more wonderful transformations in human society than the author of Aladdin ever imagined in his wildest dreams. In this short address I can of course give you but a very dim and imperfect idea of what I have called the Baconian system of experimental reasoning. Indeed, you cannot form any clear conception of it, until in some humble way you have attempted to use the method, each one for himself, and you have come here in order that you may acquire such experience. My object, however, will be gained if these illustrations serve to give emphasis to the following statements, which I feel I ought to make at the opening of these courses of instruction—statements which have an especial appropriateness in this place; since I am addressing teachers, who are in a position to exert an important influence on the system of education in this country.

In the first place, then, I must declare my conviction that no educated man can expect to realize his best possibilities of usefulness without a practical knowledge of the methods of experimental science. If he is to be a physician, his whole success will depend on the skill with which he can use these great tools of modern civilization. If he is to be a lawyer, his advancement will in no small measure be determined by the acuteness with which he can criticise the manner in which the same tools have been used by his own or his opponent's clients. If he is to be a clergyman, he must take sides in the great conflict between theology and science, which is now raging in the world, and, unless he wishes to play the part of the doughty knight Don Quixote, and think he is winning great victories by knocking down the imaginary adversaries which his ignorance has set up, he must try the steel of his adversary's blade. Let me be fully understood. It is not to be expected or desired that many of our students should become professional men of science. The places of employment for scientific men are but few, and more in the future than in the past they will naturally be secured by those whom Nature has endowed with special aptitudes or tastes—usually the signs of aptitudes—to investigate her laws. That our country will always offer an honorable career to her men of genius, we have every reason to expect, and these born students of Nature will usually follow the plain indications of Providence without encouragement or direction from us. It is different, however, with the great body of earnest students who are conscious of no special aptitudes, but who are desirous of doing the best thing to fit themselves for usefulness in the world; and I feel that any system of education is radically defective which does not comprise a sufficient training in the methods of experimental science to make the mass of our educated men familiar with this tool of modern civilization: so that when, hereafter, new conquests over matter are announced, and great discoveries are proclaimed, they may be able not

only to understand but also to criticise the methods by which the assumed results have been reached, and thus be in a position to distinguish between the true and the false. Whether we will or not, we must live under the direction of this great power of modern society, and the only question is whether we will be its ignorant slave or its intelligent servant.

In the second place, it seems fitting that I should state to you what I regard as the true aims to be kept in view in a course of scientific study, and to give my reasons for the methods we have adopted in arranging the courses you are about beginning.

In our day there has arisen a warm discussion as to the relative claims of two kinds of culture, and attempts are made to create an antagonism between them. But all culture is the same in spirit. Its object is to awaken and strengthen the powers of the mind; for these, like the muscles of the body, are developed and rendered strong and active only by exercise; while on the other hand they may become atrophied from mere want of use. Science culture differs in its methods from the old classical culture, but it has the same spirit and the same object. You must not, therefore, expect me to advocate the former at the expense of the latter; for, although I have labored assiduously during a quarter of a century to establish the methods of science teaching which have now become general, I am far from believing that they are the only true modes of obtaining a liberal education. So far from this, if it were necessary to choose one of two systems, I should favor the classical; and why?

Language is the medium of thought, and cannot be separated from it. He who would think well must have a good command of language, and he who has the best command of language I am almost tempted to say will think the best. For this reason a certain amount of critical study of language is essential for every educated man, and such study is not likely to be gained except through the great ancient languages; the advocates of classical scholarship frequently say, cannot be gained. I am not ready to accept this dictum; but I most willingly concede that in the present state of our schools it is not likely to be gained. I never had any taste myself for classical studies; but I know that I owe to the study a great part of the mental culture which has enabled me to do the work that has fallen to my share in life. But while I concede all this, I do not believe, on the other hand, that the classical is the only effective method of culture; you evidently do not think so, for you would not be here if you did. But, in abandoning the old tried method, which is known to be good, for the new, you must be careful that you gain the advantages which the new offers; and you will not gain the new culture you seek unless you study science in the right way. In the classical departments the methods are so well established, and have been so long tested by experience, that there can hardly be a wrong way. But in science there is not only a wrong

way, but this wrong way is so easy and alluring, that you will most certainly stray into it unless you strive earnestly to keep out of it. Hence I am most anxious to point out to you the right way, and do what I can to keep you in it; and you will find that our courses and methods have been devised with this object.

When advocating in our mother University of Cambridge, in Old England, the claims of scientific culture, I was pushed with an argument which had very great weight with the eminent English scholars present, and which you will be surprised to learn was regarded as fatal to the success of the science *triposes* then under debate. The argument was, that the experimental sciences could not be made the subjects of competitive examinations. Some may smile at such an objection; but, as viewed from the English stand-point, there was really a great deal in it, and the argument brought out the radical difference between scientific and classical culture. The old method of culture may be said to have culminated in the competitive examinations of the English universities. We have no such examinations here. Success depends not simply on knowing your subject thoroughly, but on having it at your fingers' ends, and those fingers so agile that they can accomplish not only a prodigious amount of work in a short time, but can do this work with absolute accuracy. For the only approach we make to an experience of this kind, we must look to our athletic contests. It may of course be doubted whether the ability, once in a man's life, to perform such mental feats, is worth what it costs. Still it implies a very high degree of mental culture, and it is perfectly certain that the experimental sciences give no field for that sort of mental prize-fights. It is easy to prepare written examinations which will show whether the students have been faithful to their work, but they cannot be adapted to such competitions as I have described without abandoning the true object of science culture. The ability of the scientific student can only be shown by long-continued work at the laboratory-table, and by his success in investigating the problems which Nature presents.

We have here struck the true key-note of the scientific method. The great object of all our study should be to study Nature, and all our methods should be directed to this one object. This aim alone will ennoble our scholarship as students, and will give dignity to our scientific calling as men of science. It is this high aim, moreover, which vindicates the worth of the mode of culture we have chosen. What is it that ennobles literary culture but the great minds which, through this culture, have honored the nations to which they belong? The culture we have chosen is capable of even greater things; not because science is nobler than art, for both are equally noble;—it is the thought, the conception, which ennobles, and I care not whether it be attained through one kind of exercise of the mental faculties or another;—but we are capable of grander and nobler thoughts than Plato,

Cicero, Shakespeare, or Newton, because we live in a later period of the world's history; when, through science, the world has become richer in great ideas. It is, I repeat, the great thought which ennobles, and it ennobles because it raises to a higher plane that which is immortal in our manhood.

If I have made my meaning clear, and if you sympathize with my feelings, you will understand why I regard culture as so important to the individual and to the nation. The works of Shakespeare and of Bacon are of more value to England to-day than the memories of Blenheim or Trafalgar; and those great minds will still be living powers in the world when Marlborough and Nelson are only remembered as historical names. I therefore believe that it is the first duty of a country to foster the highest culture, and that it should be the aim of every scholar to promote this culture both by his own efforts and his active influence. A nation can become really great in no other way. We live in a country of great possibilities; and the danger is that, as with many men I have known in college, of great potential abilities, the greatness will end where it begins. The scholars of the country should have but one voice in this matter, and urge upon the government and upon individuals the duty of encouraging and supporting mental culture for its own sake. The time has passed when we can afford to limit the work of our higher institutions of learning to teaching knowledge already acquired. Henceforth the investigation of unsolved problems, and the discovery of new truth, should be one of the main objects at our American universities, and no cost grudged, which is required to maintain at them the most active minds, in every branch of knowledge which the country can be stimulated to produce. I could urge this on the self-interest of the nation as an obvious dictate of political economy. I could say, and say truly, that the culture of science will help us to develop those latent resources of which we are so proud; will enable us to grow two blades of grass where one grew before; to extract a larger per cent. of metal from our ores; to economize our coal, and in general to direct our waiting energies so that they may produce a more abundant pecuniary reward. I could tell of Galvani studying for twenty long years to no apparent purpose the twitching of frogs' hind-legs and thus sowing the seed from which has sprung the greatest invention of modern times. Or, if our Yankee impatience would be unwilling to wait half a century for the fruit to ripen, I could point to the purely theoretical investigations of organic chemistry, which in less than five years have revolutionized one of the great industries of Europe, and liberated thousands of acres for a more beneficent agriculture. This is all true, and may be urged properly if higher considerations will not prevail. It is an argument I have used in other places, but I will not use it here; although I gladly acknowledge the Providence which brings at last even material fruits to re-

ward conscientious labor for the advancement of kuowledge and the intellectual elevation of mankind. I would rather point to that far greater multitude who worked in faith for the love of knowledge, and who ennobled themselves and ennobled their nation, not because they added to its material prosperity, but because they made themselves and made their fellows more noble men.

I come back now again to the moral of all this, to urge upon you, as the noblest patriotism and the most enlightened self-interest, the duty of striving for yourselves and encouraging in others the highest culture in the studies you have chosen, and this culture with one end in view to advance knowledge. I am far, of course, from advising you to grapple immaturely with unsolved problems, or, when you have gained the knowledge with which you can dare to venture from the beaten track, to undertake work beyond your power. Many a young scientific man has suffered the fate of Icarus in attempting to soar too high. Moreover, I am far from expecting that all or many of you will ever have the opportunity of going beyond the well-explored fields of knowledge; but you can all have the aim, and that aim will make your work more worthy and more profitable to yourselves. Every American boy cannot be President of the United States, but if, as our English cousins allege, he believes that he can be, the very belief makes him an abler man.

We have dwelt long enough on these generalities, and it is time to come down to commonplaces, and to inquire what are the essential conditions of this scientific culture which shall fit us to investigate Nature; and the first thought that occurs to me in this connection may be expressed thus: Science presents to us two aspects, which I may call its objective and its subjective aspect. Objectively it is a body of facts, which we have to observe, and subjectively it is a body of truths, conclusions, or inferences, deduced from these facts; and the two sides of the subject should always be kept in view. I propose next to say a few words in regard to each of these two aspects of our study, and in regard to the best means of training our faculties so as to work successfully in each sphere. First, then, success in the observation of phenomena implies three qualities at least, namely, quickness and sharpness of perception, accuracy in details, and truthfulness; and on its power to cultivate these qualities a large part of the value of science, as a means of education, depends. To begin with the cultivation of our perceptions. We are all gifted with senses, but how few of us use them to the best advantage! "We have eyes and see not;" for, although the light paints the picture on the retina, our dull perceptions give no attention to the details, and we retain only a confused impression of what has passed before our eyes. "But how," you may ask, "are we to cultivate this sharpness of perception?" I answer, only by making a conscious effort to fix our attention on the objects we study, until the habit becomes a second nature. I have often noticed,

with surprise, the power which uneducated miners frequently possess, of recognizing many minerals at sight. This they have acquired by long experience and close familiarity with such objects, and such power of observation is with them so purely a habit that they are frequently unable to state clearly the grounds on which their conclusions are based. They recognize the minerals by what in common language is called their *looks*, and they notice delicate differences in the *looks* to which most men are blind. It is, however, the business of the scientific mineralogist to analyze these *looks*, and to point out in what the differences consist; so that by fixing his attention on these points the student may gain, by a few hours' study, the power which the miner acquires only after long experience. The chief difficulty, however, which we find in teaching mineralogy is, that the students do not readily see the differences when they are pointed out, or, if they see them, do not remember them with sufficient precision to render their subsequent observations conclusive and precise. This either arises from a failure to cultivate the powers of observation in childhood, or the subsequent blunting of them by disuse. The ladies will scout the idea that a brooch of cut-glass is as ornamental as one of diamond, and yet I venture to assert that there is not one person in fifty, at least of those who have not made a study of the subject, who can tell the difference between the two. The external appearance depends simply on what we call lustre. The lustre of glass is vitreous, that of the diamond adamantine, and I know of no other distinction which it is more difficult for students to recognize than this. Those of you who study mineralogy will experience this difficulty, and it can be overcome only by giving careful attention to the subject. The teacher can do nothing more than put in your hands the specimens which illustrate the point, and you must study these specimens until you see the difference. It is a question of sight, not of understanding, and all the optical theories of the cause of the lustre will not help you in the least toward seeing the difference between diamond and glass, or anglesite and heavy spar. Another illustration of the same fact is the constant failure of students to distinguish by the eye alone between the two minerals called copper-glance and gray copper. There is a difference of color and lustre which, although usually well marked, it requires an educated eye to distinguish.

Mineralogy undoubtedly demands a more careful cultivation of the perceptions than the other branches of chemistry; but still you will find abundant practice for close observation in them all. I have often known students to reach erroneous results in qualitative analysis by mistaking a white precipitate in a colored liquid for a colored precipitate; or by not attending to similar broad distinctions which would have been obvious to any careful observer; and so in quantitative analysis, mere delicacy of touch or handling is a great element of success.

But I must pass on to speak of the importance in the study of Nature of accuracy in detail, which is the second condition of successful observation of which I spoke. We must cultivate not only accuracy in observing details, but also accuracy in following details which have been laid down by others for our guidance. In science we cannot draw correct conclusions from our premises unless we are sure that we have all the facts, and what seemed at first an unimportant detail often proves to be the determining condition of the result; and, again, if we are told that under certain conditions a certain sign is the proof of the presence of a certain substance, we have no right to assume that the sign is of any value unless the conditions are fulfilled. A black precipitate, for example, obtained under certain conditions, is a proof of the presence of nickel, but we cannot assert that we have found nickel unless we have followed out those details in every particular. Of course, we must avoid empiricism as far as we can. We must seek to learn the reasons of the details, and such knowledge will not only render our works intelligent, but will also frequently enable us to judge how far the details are essential, and to what extent our processes may be varied with safety. We must also avoid trifling, and above all "the straining at a gnat and swallowing a camel," as is the habit with triflers. Large knowledge and good judgment will avoid all such errors; but, if we must choose between fussiness and carelessness, the first is the least evil. Slovenly work means slovenly results, and habits of carefulness, neatness, and order, produce as excellent fruits in the laboratory as in the home.

Last in order but first in importance of the conditions of successful observation, mentioned above, stands truthfulness. Here you may think I am approaching a delicate subject, of which even to speak might seem to cast a reproach. But not so at all. I am not speaking here of conscious deception, for I assume that no one who aspires to be a student of Nature can be guilty of that. But I am speaking of a quality whose absence is not necessarily a mark of sinfulness, but whose possession, in a high degree, is a characteristic of the greatest scientific talent. As every lawyer knows, he is a rare man whose testimony is not colored by his interests, and a very large amount of self-deception is compatible with conscious honesty of purpose. So among scientific students the power to keep the mind unbiased and not to color our observations in the least degree, is one of the rarest as it is one of the noblest of qualities. It is a quality we must strive after with all our might, and we shall not attain it unless we strive. Remember, our observations are our data, and, unless accurate, every thing deduced from them must have the taint of our deception. We cannot deceive Nature, however much we may deceive ourselves; and there is many a student who would cut off his right hand rather than be guilty of a conscious untruth, who is yet constantly untruthful to himself. Every year students of mineralogy present to me written descriptions of

mineral specimens which particularize, as observed, characters that do not appear on the specimens given them to determine, although they may be the correct characters of some other mineral. There is usually no want of honesty in this, but, deceived by some accident, the student has made a wrong guess, and then imagined that he saw on the specimen those characters which he knew from the descriptions ought to appear on the assumed mineral. So, also, it not unfrequently happens that a student in qualitative analysis, who has obtained some hints in regard to the composition of his solution, will torture his observations until they seem to him to confirm his erroneous inferences; and again the student in quantitative analysis, who finds out the exact weight he ought to obtain, is often insensibly influenced by this knowledge—in the washing and ignition of his precipitate, or in some other way—and thus obtains results whose only apparent fault may be a too close agreement with theory, but which, nevertheless, are not accurate because not true. It is evident how fatal such faults as these must be to the investigation of truth, and they are equally destructive of all scientific scholarship. Their effect on the student is so marked that although he may deceive himself, he will rarely deceive his teacher. That he should lose confidence in his own results is, to the teacher, one of the most marked indications of such false methods of study, but the student usually refers his want of success to any cause but the real one—his own untruthfulness. He will complain of the teacher, or of the methods of instruction, and may even persuade himself that all scientific results are as uncertain as his own. As I have said, mere ordinary truthfulness, which spurns any conscious deception, will not save us from falling into such faults. Our scientific study demands a much higher order of truthfulness than this. We should so love the truth above all price as to strive for it with single-hearted and unswerving purpose. We must be constantly on our guard to avoid any circumstance which would tend to bias our minds or warp our judgments, and we must make the attainment of the truth our sole motive guide and end.

It remains for me, before closing this address, to say a few words on what I have called the subjective aspect of scientific study. Science offers us not only a mass of phenomena to be observed, but also a body of truths which have been deduced from these observations; and, without the power of drawing correct inferences from the data acquired, exact observations would be of little value. I have already described the inductive method of reasoning, and illustrated it by two noteworthy examples, and, in a humbler measure, we must apply the same method in our daily work in the laboratory. We must learn how to vary our experiments so as to eliminate the accidental circumstances, and make evident the essential conditions of the phenomena we are studying. Such power can only be acquired by practice, and a somewhat long experience in active teaching has convinced me that

there is no better means of training this logical faculty than the study of qualitative chemical analysis in which many of you are to engage. The results of the processes of qualitative analysis are perfectly definite and trustworthy; but they are only reached by following out the indications of experiments which are frequently obscure, and even apparently contradictory; reconciling by new experiments the seeming discrepancies, and, at last, having eliminated all other possible causes of the phenomena observed, discovering the true nature of the substances under examination. The study of mineralogy affords an almost equally good practice, although in a somewhat different form. By comparing carefully many specimens of the same mineral, you learn to distinguish the accidental from the essential characters, and on this distinction you must base your inferences in regard to the nature of the specimens you may be called upon to determine. A single remark occurs to me which may aid you in cultivating this scientific logic.

Do not attempt to reason on insufficient data. Multiply your observations or experiments, and, when your premises are ample, the conclusion will generally take care of itself. Are you in doubt in regard to a mineral specimen? Repeat your observations again and again, multiply them with the aid of the blow-pipe or goniometer, compare the specimen with known specimens which it resembles, until either your doubts are removed, or you are satisfied that you are unequal to the task; and remember that, in many cases, the last is the only honest conclusion. Are you in doubt in regard to the reactions of the substance you are analyzing, whether they are really those of a metal you suspect to be present? Do not rest in such a frame of mind, and, above all, do not try to remove the doubt by comparing your experience with that of your neighbor: but multiply your own experiments; procure some compound of the metal, and compare its reactions with those you have observed, until you reach either a positive or a negative result. Remember that the way to remove your doubts is to widen your own knowledge, and not to depend on the knowledge of others. When your knowledge of the facts is ample, your inferences will be satisfactory, and then an unexplained phenomenon is the guide to a new discovery. Do not be discouraged if you have to labor long in the dark before the day begins to dawn. It will at last dawn to you, as it has dawned to others before, and, when the morning breaks, you will be satisfied with the result of your labor.

Moreover, I feel confident that such experience will very greatly tend to increase your appreciation of the value of scientific studies in training the reasoning faculties of the mind. This, as every one must admit, is the best test of their utility in a scheme of education, and it is precisely here that I claim for them the very highest place. It has generally been admitted that mathematical studies are peculiarly well adapted to train the logical faculties, but still many persons have maintained that, since the mathematics deal wholly with absolute certain-

ties, an exclusive devotion to this class of subjects unfits the mind for weighing the probable evidence by which men are chiefly guided in the affairs of life. But, without attempting to discuss this question, on which much might be said on both sides, it is certain that no such objection can be urged against the study of the physical sciences if conducted in the manner I have attempted to describe. These subjects present to the consideration of the student every degree of probable evidence, accustoming him to weigh all the evidence for or against a given conclusion, and to reject or to provisionally accept only on the balance of probabilities. Moreover, in practical science, the student is taught to follow out a chain of probable evidence with care and caution, to eliminate all accidental phenomena, and supply, by experiment or observation, the missing links, until he reaches the final conclusion—an intellectual process which, though based wholly on probable evidence, may have all the force and certainty of a mathematical demonstration. Indeed, that highly-valued scientific acumen and skill which enables the student to brush away the accidental circumstances by which the laws of Nature are always concealed until the truth stands out in bold relief, is but a higher phase of the same talent which marks professional skill in all the higher walks of life. The physician who looks through the external symptoms of his patient to the real disease which lurks beneath; the lawyer, who disentangles a mass of conflicting testimony, and follows out the truth successfully to the end; the statesman, who sees beneath the froth of political life the great fundamental principles which will inevitably rule the conduct of the State, and thus foresees and provides for the coming change; the general, who discovers amid the confusion of the battle-field the weak point of his enemy's front; the merchant, even, who can interpret the signs of the unsettled market—employ the same faculty, and frequently in not a much lower degree, that discovered the law of gravitation, and which, since the days of Newton, has worked so successfully to unveil the mysteries of the material creation.

Moreover, I hope, my friends, that you will come to value scientific studies, not simply because they cultivate the perceptive and reasoning faculties, but also because they fill the mind with lofty ideals, elevated conceptions, and noble thoughts. Indeed, I claim that there is no better school in which to train the æsthetical faculties of the mind, the tastes, and the imagination, than the study of natural science. The beauty of Nature is infinite, and the more we study her works the more her loveliness unfolds. The upheaved mountain, with its mantle of eternal snow; the majestic cataract, with its whirl and roar of waters; the sunset cloud, with its blending of gorgeous hues, lose nothing of their beauty for him who knows the mystery they conceal. On the contrary, they become, one and all, irradiated by the Infinite Presence which shines through them, and fill the mind with grander conceptions and nobler ideas than your uneducated child of Nature could ever attain. Remember that I am not recommending an exclu-

sive devotion to the natural sciences. I am only claiming for them their proper place in the scheme of education, and I do not, of course, deny the unquestionable value of both the ancient and the modern classics in cultivating a pure and elevated taste. But I do say that the poet-laureate of England has drawn a deeper inspiration from Nature interpreted by science than any of his predecessors of the classical school; and I do also affirm that the pre-Raphaelite school of painting, with all its grotesque mimicry of Nature, embodies a truer and purer ideal than that of any Roman fable or Grecian dream. And what shall we say of the imagination? Where can you find a wider field for its exercise than that opened by the discoveries of modern science? And as the mind wanders over the vast expanse, crossing boundless spaces, dwelling in illimitable time, witnessing the displays of immeasurable power, and studying the adaptations of Omniscient skill, it lives in a realm of beauty, of wonder, and of awe, such as no artist has ever attained to in word, in sound, in color, or in form. And if such a life does not lead man to feel his own dependence, to yearn toward the Infinite Father, and to rest on the bosom of Infinite Love, it is simply because it is not the noble in intellect, not the great in talent, not the profound in knowledge, not the rich in experience, not the lofty in aspiration, not the gifted in imagery, but solely the pure in heart, who see God.

Such, then, is a very imperfect presentation of what I believe to be the value of scientific studies as a means of education. In what I have stated I have implied that, for these studies to be of any real value, the end must be constantly kept in view, and every thing made subservient to the one great object. To study the natural sciences merely as a collection of interesting facts which it is well for every educated man to know, seldom serves a useful purpose. The young mind becomes wearied with the details, and soon forgets what it has never more than half acquired. The lessons become an exercise of the memory and of nothing more; and if, as is too frequently the case, an attempt is made to cram the half-formed mind in a single school-year with an epitome of half the natural sciences—natural philosophy, astronomy, and chemistry, physiology, zoölogy, botany, and mineralogy, following each other in rapid succession—these studies become a great evil, an actual nuisance, which I should be the first to vote to abate. The tone of mind is not only not improved, but seriously impaired, and the best product is a superficial, smattering smartness, which is the crying evil not only of our schools, but also of our country. In order that the sciences should be of value in our educational system, they must be taught more from things than from books, and *never* from books without the things. They must be taught, also, by real living teachers, who are themselves interested in what they teach, are interested also in their pupils, and understand how to direct them aright. Above all, the teachers must see to it that their pupils study with

the understanding and not solely with the memory, not permitting a single lesson to be recited which is not thoroughly understood, taking the greatest care not to load the memory with any useless lumber, and eschewing *merely* memorized rules as they would deadly poison. The great difficulty against which the teachers of natural science have to contend in the colleges are the wretched tread-mill habits the students bring with them from the schools. Allow our students to memorize their lessons, and they will appear respectably well, but you might as easily remove a mountain as to make many of them think. They will solve an involved equation of algebra readily enough so long as they can do it by turning their mental crank, when they will break down on the simplest practical problem of arithmetic which requires of them only thought enough to decide whether they shall multiply or divide. Many a boy of good capabilities has been irretrievably ruined, as a scholar, by being compelled to learn the Latin grammar by rote at an age when he was incapable of understanding it; and I fear that schools may still be found where young minds are tortured by this stupefying exercise. Those of us who have faith in the educational value of scientific studies are most anxious that the students who resort to our colleges should be as well fitted in the physical sciences as in the classics, for otherwise the best results of scientific culture cannot be expected. As it is, our students come to the university, not only with no preparation in physical science, but with their perceptive and reasoning faculties so undeveloped that the acquisition of the elementary principles of science is burdensome and distasteful: and good scholars, who are ambitious of distinction, can more readily win their laurels on the old familiar track than on an untried course of which they know nothing, and for which they must begin their training anew. We have improved our system of instruction in the college as fast as we could obtain the means, but we are persuaded that the best results cannot be reached without the coöperation of the schools. We feel, therefore, that it is incumbent upon us, in the first place, to do every thing in our power to prove to the teachers of this country how great is the educational value of the physical sciences, when properly taught; and, secondly, to aid them in acquiring the best methods of teaching these subjects. It is with such aims that our summer courses have been instituted, and your presence here in such numbers is the best evidence that they have met a real want of the community. We welcome you to the university and to such advantages as it can afford, and we shall do all in our power to render your brief residence here fruitful both in experience and in knowledge; hoping also that the university may become to you, as she has to so many others, a bright light shining calmly over the troubled sea of active life, ever suggesting lofty thoughts, encouraging noble endeavors, and inciting all her children to work together toward those great ends, the advancement of knowledge and the education of mankind.

THE NOBILITY OF KNOWLEDGE.[1]

By JOSIAH P. COOKE, Jr.,
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WITHIN a comparatively few years schools for the instruction of artisans have become a prominent feature in the educational systems both of this country and of Europe, and seem destined to supersede the old system of apprenticeships. The establishment of these schools has been an important step in human progress, not because any great advantage has been gained in the cultivation of mechanical skill, but because here the future mechanic acquires culture of the mind as well as skill of the hand. Indeed, it may be doubted whether our utilitarian age can ever successfully compete with those "elder days of art" when

> "Builders wrought with greatest care,
> Each minute and unseen part."

But, if our industrial schools do not make better mechanics than the workshops of the olden time, they certainly educate better men, and, by adding to skill, knowledge, they are elevating the mechanic and ennobling his calling.

If, therefore, these schools are the representatives in our age of the workshops with their bands of apprentices in the days of yore, then that by which the schools are distinguished, that which they have added to the old system, is not art but mental culture; and therefore, when asked to address you on this occasion, I could think of no more appropriate subject than the Nobility of Knowledge. Identified with an institution in which mental culture is the chief aim, I felt that I was asked to address a body of cultivated working-men with whom, though employed in the mechanic arts, the acquisition of knowledge was also a privilege and a pride. I felt, moreover, that a proper appreciation of the true dignity of knowledge, in itself considered, and apart from all economical considerations, is one of the great wants of our age and of our country.

Knowledge is power. Knowledge is wealth. These trite maxims

[1] An address delivered before the Free Institute at Worcester, Mass., July 28, 1874.

are sufficiently esteemed in our community, and need not that they be enforced by any one. So far as knowledge will yield immediate distinction or gain, it is sought and fostered by multitudes. But when the aim is low the attainment is low, and too many of our students are satisfied with superficiality, if it only glitters, and with charlatanry, if it only brings gold.

Let me not be understood to depreciate the material advantages of learning. I rejoice that in this world knowledge frequently yields wealth and fame, and I should have little hope for human progress were the prizes of scholarship less than they are. Power and wealth are noble aims, and when rightly used may be the means of conferring unmeasured blessings on mankind; but I desire at this time to impress upon you, my friends, the fact that knowledge has nobler fruits than these, and that the worth of your knowledge is to be measured not by the credits it will add to your account in the ledger or the position it may give you among men, but by the extent to which it educates your higher nature, and elevates you in the scale of manhood.

I address young men who are just entering on life, who are at an age when the mystery of our being usually presses most closely upon the soul, and whose aspirations for higher culture and clearer vision have not been deadened by the sordid damps of the world. Trust no croakers who tell you that your youthful visions are illusions, which a little contact with the real business of the world will dispel. It is only too true that these visions will become fainter and fainter, if you allow the cares of the world to engross your thoughts; but, unless your higher nature becomes wholly deadened, you will look back to the time when the visions were brightest, as the golden period of your life, and let me assure you that, if you only are true to the aspirations of your youth, they will become clearer and clearer to the last, and, as we firmly believe, will prove to be the dawn of the perfect day.

My friends, if you have seen these visions, "the nobility of knowledge" has been a reality of your experience. You know that there is a life lived in communion with the thoughts of great men or with the thoughts of God as we can read them in Nature and Revelation, which is purer and nobler than a life of money-making or political intrigue, and I would that I could so bring you to appreciate not only the nobility, but also the happiness, of such a life as to induce you to try to live it. Do you tell me that it is only granted to a few men to become scholars, and that you have been educated for some industrial pursuit? But remember, as I said before, that it is your special privilege to have been educated, to have added knowledge to your handicraft, and that this very knowledge, if kept alive so far as you are able, will ennoble your life. Knowledge, like the fairy's wand, ennobles whatever it touches. The humblest occupations are adorned by it, and without it the most exalted positions appear to true men mean and low.

Nor is it the extent of the knowledge, alone, which ennobles, but much more the spirit and aim with which it is cultivated, and that spirit and aim you may carry into any occupation however engrossing, and into any condition of life however obscure.

And let me add that what I have said is true not only of the individual, but also, and to an even greater degree, of the nation. Our people, for the most part, look upon universities and other higher institutions of learning as merely schools for recruiting the learned professions, and estimate their efficiency solely by the amount of teaching-work which they perform. But, however important the teaching function of the university may be, I need not tell you that this is not its only or chief value to a community. The university should be the centre of scientific investigation and literary culture, the nursery of lofty aspirations and noble thoughts, and thus should become the soul of the higher life of the nation. For this and this chiefly it should be sustained and honored, and no cost and no sacrifice can be too great, which is required to maintain its efficiency. And its success should be measured by the amount of knowledge it produces rather than by the amount of instruction it imparts.

Harvard College, by cherishing and honoring the great naturalist she has recently lost, has done more for Massachusetts than by educating hosts of commonplace professional men. The simple title of teacher, which in his last will Louis Agassiz wrote after his name, was a nobler distinction than any earthly authority could confer; but remember he was a teacher not of boys, but of men, and his influence depended not on the instruction in natural history which he gave in his lecture-room, but on his great discoveries, his far-reaching generalization, and his noble thoughts. Although that man died poor, as the world counts poverty, yet the bequest which he left to this people cannot be estimated in coin.

It is a sorry confession to make, but it is nevertheless the truth, that, if we compare our American universities, in point of literary or scientific productiveness, with those of the Old World, they will appear lamentably deficient. Let me add, however, that this deficiency arises not from any want of proper aims in our scholars, but simply from the circumstance that our people do not sufficiently appreciate the value of the higher forms of literary and scientific work to bear the burden which the production necessarily entails. Scholars must live, as well as other men, and in a style which is in harmony with their surroundings and cultivated tastes, and their best efforts cannot be devoted to the extension of knowledge unless they are relieved from anxiety in regard to their daily bread.

In our colleges the professors are paid for teaching and for teaching only, while in a foreign university the teaching is wholly secondary, and the professor is expected to announce in his lectures the results of his own study, and not the thoughts of other men. Until the whole

status of the professors in our chief universities can be changed, very little original thought or investigation can be expected, and these institutions cannot become what they should be, the soul of the higher life of the nation. It is in your power, however, to bring about this change, but the reform can be effected in only one way. You must give to your universities the means of supporting fully and generously those men of genius who have shown themselves capable of extending the boundaries of human knowledge, and demand of them, *only*, that they devote their lives to study and research, and let me assure you that no money can be spent which will yield a larger or more valuable return.

If you do not look beyond your material interests, the higher life of the nation, which you will thus serve to cherish and foster, will guard your honor, and protect your home; and, on the other hand, what can you expect in a nation whose highest ideal is the dollar, or what the dollar will buy, but venality, corruption, and ultimate ruin?

But, rising at once to the noblest considerations, and regarding only the welfare of your country and the education of your race, what higher service can you render than by sustaining and cherishing the grandest thought, the purest ideals, and the loftiest aspirations, which humanity has reached, and making your universities the altars where the holy fire shall be kept ever burning bright and warm?

Do you think me an enthusiast? Look back through history, and see for yourselves what has made the nations great and glorious. Why is it that, after twenty centuries, the memory of ancient Greece is still enshrined among the most cherished traditions of our race? Is it not because Homer sang, Phidias wrought, and Plato, Aristotle, Demosthenes, Thucydides, with a host of others, thought and wrote? Or, if for you the military exploits of that classic age have the greater charm, do not forget that, were it not for Grecian literature, Thermopylæ, Marathon, and Salamis, would have been long since forgotten, and that the bravery, self-devotion, and patriotism, which these names embalm, were the direct fruits of that higher life which those great thinkers illustrated and sustained. And, coming down to modern times, what are the shrines in our mother-country which we chiefly venerate, and to which the transatlantic pilgrim oftenest directs his steps? Is it her battle-field, her castles and baronial halls, or such spots as Stratford-on-Avon, Abbotsford, and Rydal Mount? Why, then, will we not learn the lesson which history so plainly teaches, and strive for those achievements in knowledge and mental culture which will be remembered with gratitude when all local distinctions and political differences shall have passed away and been forgotten?

While I was considering the line of discourse which I should follow on this occasion, an incident occurred suggesting an historical parallel, which will illustrate, better than any reflections of mine, the

truth I would enforce. The ship Faraday arrived on our coast after laying over the bed of the Atlantic another of those electric nerves through which pulsate the thoughts of two continents, and, as I read the description of that noble ship, fitted out with all the appliances which modern science had created to insure the successful accomplishment of the enterprise, I remembered that not a century had elapsed since the first obscure phenomena were observed, whose conscientious study, pursued with the unselfish spirit of the scientific investigator, had led to these momentous results, and my imagination carried me back to an autumn day of the year 1786, in the old city of Bologna, in Italy, and I seemed to assist at the memorable experiment which has associated the name of Aloysius Galvani with that mode of electrical energy which flashes through the wire-cords that now unite the four quarters of the globe.

Galvani is Professor of Anatomy in the University of Bologna, and there is hanging from the iron balcony of his house a small animal preparation, which is not an unfamiliar sight in Southern Europe, where it is regarded as a delicacy of the table. It is the hind-legs of a frog, from which the skin had been removed, and the great nerve of the back exposed. Six years before, his attention had been called to the fact that the muscles of the frog were convulsed by the indirect action of an electrical machine, under conditions which he had found very difficult to interpret. He had connected the phenomenon with a theory of his own: that electricity—that is, common friction electricity, the only mode of electrical action then known—was the medium of all nervous action; and this had led him into a protracted investigation of the subject, during which he had varied the original experiment in a thousand ways, and he had now suspended the frog's legs to the iron balcony, in order to discover if atmospheric electricity would have any effect on the muscles of the animal.

Galvani has spent a long day in fruitless watching, when, while holding in his hand a brass wire, connected with the muscles of the frog, he rubs the end, apparently listlessly, against the iron railing, when, lo! the frog's legs are convulsed.

The patient waiting had been rewarded, for this observation was the beginning of a line of discovery which was ere long to revolutionize the world. But Galvani was not destined to follow far the new path he had thus opened. The remarkable fact observed was this: The convulsions of the frog's legs could be produced without the intervention of electricity, or, at least, of the one kind of electricity then known, and Galvani soon found out that the only condition necessary to produce the result was, that the nerve of the frog should be connected with the muscle of the leg by some good electrical conductor. But, although Galvani followed up this observation with the greatest zeal, and showed remarkable sagacity throughout his whole investigation, yet he was too strongly wedded to his own theory to

interpret correctly the facts he observed. He supposed, to the end of his life, that the whole effect was caused by animal electricity flowing through the conductor from the nerve to the muscle, and his experiments were chiefly interesting to himself and to his contemporaries, from the light they were supposed to throw on the mysterious principle of life. We now know that animal electricity played only a small part in the phenomena he observed, and that the chief effects were due to a cause of which he was wholly ignorant.

Galvani published his observations in 1791, in a monograph entitled "The Action of Electricity in Muscular Motion." This publication excited the most marked attention, and, within a year, all Europe was experimenting on frogs' legs. The phenomena were everywhere reproduced, but Galvani's explanation of the phenomena was by no means so universally accepted. His theory was controverted in many quarters, and by no one more successfully than by Alexander Volta, Professor of Physics in the neighboring University of Pavia. Volta, while admitting, with Galvani, that the muscular contractions were caused by electricity, explained the origin of the electricity in a wholly different way. According to Volta, the electricity originated not in the animal, but in the contact of the dissimilar metals, or other materials used in the experiment. This difference of opinion led to one of the most remarkable controversies in the history of science, and for six years, until his death in 1798, Galvani was occupied in defending his theory of animal electricity against the assaults of his distinguished countryman.

This discussion created the liveliest interest throughout Europe. Every scholar of science took sides with one or the other of these eminent Italian philosophers, and the scientific world became divided into the school of Galvani and the school of Volta. Yet, so far at least as the fundamental experiment was concerned, both were wrong. The electricity came neither from the body of the frog nor from the contact of dissimilar kinds of matter, but was the result of chemical action, which both had equally overlooked. But, nevertheless, the controversy led to the most important results: for Volta, while endeavoring to sustain his false theory by experimental proofs, was led to the discovery of the *voltaic* pile, or, as we now call it, the *voltaic* battery, an instrument whose influence on civilization can be compared only with the printing-press and the steam-engine. Yet, although the whole action of the battery was in direct contradiction to his pet theory, still, to the last, Volta persistently defended the erroneous doctrine he had espoused in his controversy with Galvani thirty years before, and he died in 1827, without realizing how great a boon he had been instrumental in conferring on mankind; so true it is, that Providence works out her bright designs even through the blindness and mistakes of man.

But there is another lesson to be learned from this history, which

cannot be too often rehearsed in this self-sufficient age, which boasts so proudly of its practical wisdom. There were, doubtless, many practical men in that city of Bologna to smile at their sage professor who had spent ten long years in studying, to little apparent purpose, the twitchings of frogs' hind-legs, and there was many a jest among the courtiers of Europe at the expense of the learned philosophers who "wasted" so much time in discussing the cause of such trivial phenomena. But how is it now?

Less than a century has passed since Galvani's death; and, in a small hut, on the shores of Valentia Bay, may be seen one of the most skillful of a new class of *practical men*, representing a profession which owes its origin to Galvani and Volta. This *electrician* is watching a spot of light on the scale of an instrument which is called a *galvanometer*. Since the fathers fell asleep, the field of knowledge which they first entered has spread out wider and wider before the untiring explorers who have succeeded them. Oersted and Seebeck, Arago and Ampère, Faraday and our own Henry, have made wonderful discoveries in that field; and other great men, like Steinheil, Wheatstone, Morse, and Thomson, have invented ingenious instruments and appliances, by which these discoveries might be made to yield great practical results.

The spot of light, which the electrician is watching, is reflected from one of the latest of these inventions—the reflecting galvanometer of Thomson. He and his assistants had been watching by turns the same spot for several days, since the Great Eastern had steamed from the bay, paying out a cable of insulated wire. These electricians had no anxiety as to the result, for daily signals had been exchanged between the ship and the shore, as hundreds after hundreds of miles of this electrical conductor had been laid on the bed of the broad ocean. The coast of Newfoundland had already been reached, and they were only waiting for the landing of the cable at the now far-distant end.

At length the light quivers, and the spot begins to move! It answers to concerted signals! And soon the operator spells out the joyful message. The ocean has been spanned with an electric nerve, and the New World responds to the greetings of the Old.

Here is something practical, which all can appreciate, and all are ready to honor. We honor the courage which conceived, the skill which executed, and, above all, the success which crowned the undertaking. But, do we not forget that professor of Bologna with his frogs' legs, who sowed the seed from which all this has sprung? He labored without hope of temporal reward, stimulated by the pure love of truth; and the grain which he planted has brought forth this abundant harvest. Do we not forget, also, that succession of equally noble men, Volta, and Oersted, and Faraday, with many other not less devoted investigators of electrical science, without whose unselfish

labors the great result never could have been achieved? Such men, of course, need no recognition at our hands, and I ask the question not for their sakes, but for ours. The intellectual elevation of the lives they led was their all-sufficient reward.

It is, however, of the utmost importance for us, citizens of a country with almost unlimited resources, that we should recognize what are the real springs of true national greatness and enduring influence. In this age of material interests, the hand is too ready to say to the head, "I have no need of thee," and, amid the ephemeral applause which follows the realization of some triumph over matter, we are apt to be deceived, and not observe whence the power came. We associate the great invention with some man of affairs who overcame the last material obstacle, and who, although worthy of all praise, probably added very little to the total wealth of knowledge, of which the invention was an immediate consequence; and, not seeing the antecedents, we are apt to underrate the part which the student or scientific investigator may have contributed to the result.

It is idle, for example, to speak of the electric telegraph as invented by any single man. It was a growth of time; and many of the men who contributed to win this great victory of mind over space "builded far better than they knew." As I view the subject, that invention is as much a gift of Providence as if the details had been supernaturally revealed. But, whatever may be our speculative views, it is of the utmost importance to the welfare of our community that we should realize the fact that purely theoretical scientific study, pursued for truth's sake, is the essential prerequisite for such inventions. *Knowledge is the condition of invention.* The old Latin word *invenio* signifies *to meet with*, or *to find*, and these great gifts of God are *met with* along the pathway of civilization; but the throng of the world passes them unnoticed, for only those can recognize the treasure whose minds have been stored with the knowledge which the scholar has discovered and made known.

If, then, as no one will deny, science and scholarship are the powers by which improvements in the useful arts are made, I might appeal to your self-interest to support and cherish them. But I should despise myself for appealing to such a motive, and you for requiring it. The supreme importance of science and scholarship to a nation does not depend in the least on the circumstance that important practical results may follow. When, as in the case of Galvani's frogs, they come in the order of Providence, let us thank God for them as a gift which we had no right either to expect or demand. Science, if studied successfully, must be studied for the pure love of truth; and, if we serve her solely for mercenary ends, her truths, the only gold she offers, will turn to dross in our hands, and we shall degrade ourselves in proportion as we dishonor her. Galvani, and Volta, and Oersted, who discovered the truths of which the electric telegraph is a simple applica-

tion, sure to be made as soon as the time was ripe, are not the less to be honored because they died before the fullness of that time had come. We honor them for the truths they discovered, and the lustre of their consecrated lives could be neither enhanced nor impaired by subsequent events; and it is because I am persuaded that such lives are the salt of the world, the saviors of society, that I would lead you to cherish and sustain them; and, that I may enforce this conclusion, allow me to ask your attention to another historical incident, which presents a striking parallelism to the last.

I must take you back to a period which we, of a nation born but yesterday, regard as distant, but which was one of the most noted epochs of modern history—the age of Luther and the Reformation. I must ask you to accompany me to the small town of Allenstein, near Frauenberg, in Eastern Prussia, where, on the 23d of May, 1543, there lay dying one of the great benefactors of mankind. This man, old at seventy years, "bent and furrowed with labor, but in whose eye the fire of genius was still glowing," was then known as one of the most learned men of his time. Doctor of Medicine as well as of Theology, Canon of Frauenberg, Honorary Professor of Bologna and Rome, while devoting his leisure to study, he had passed a life of active benevolence in administering to the bodily as well as the spiritual wants of the ignorant people among whom his lot had been cast. He was also a great mechanical genius, and, by various labor-saving machines, of his own invention, he had contributed greatly to the welfare of the surrounding country; but the superstitious peasants, although they had hitherto reverenced the great man as their best friend and benefactor, had been recently incited by his enemies and rivals in the Church to curse him as a heretic and a wizard. A few days back he had been the unwilling witness of one of those out-of-door spectacles, so common at that time, in which his scientific opinions had been travestied, his charities ridiculed, and his devoted life made the object of slander and reproach. This ingratitude of his flock had broken his heart, and he could not recover from the blow.

The occasion of this outburst of fanaticism was the approaching publication of a work in which he had dared to question the received opinions of theologians and schoolmen, in regard to cosmogony. He had, forsooth, denied that the visible firmament was a solid azure-colored shell, to which the sun and planets were fastened, and through whose opened doors the rain descended. He had proved that the sun was the centre of the system, around which the earth and planets revolved, and, with his clear scientific vision, he had been able to gain glimpses, at least, of the grand conceptions of modern astronomy: For this man was Nicolas Copernicus, and the expected book was his great work—"De Orbium Cœlestium Revolutionibus"—destined to form the broad basis of astronomical science. The work was

printing at Nuremberg, and the last proofs had been returned; but reports had come that a similar outburst of fanaticism was raging at that place, that a mob had burnt the manuscript on the public square, and had threatened to break the press should the printing proceed. But, thanks to God! the old man was not to die before the hour of triumph came. While still conscious, a horse, covered with foam, gallops to the door of his humble dwelling, and an armed messenger enters the chamber, who, breathless with haste, places in the hands of the dying man a volume still wet from the press. He has only strength to return a smile of recognition, and murmur the last words:

"Nunc dimittis servum tuum, Domine."

Grand close of a noble life! The seed has been sown—what could we desire more?

Again the centuries roll on—not one, but three; while the seed grows to a great tree, which overshadows the nations. Great minds have never been wanting to cherish and prune it, like Tycho Brahe and Kepler, Galileo and Newton, Laplace and Lagrange; and although at times some, while lingering in the deep shade of the foliage, may have lost sight of the summit, the noble tree has ever pointed upward to direct aspiration and encourage hope.

On the evening of the 24th of September, 1846, in the Observatory of Berlin, a trained astronomical observer was carefully measuring the position of a faint star in the constellation Capricorn. Only the day before, he had received from Le Verrier a letter announcing the result of that remarkable investigation which has made the name of this distinguished French astronomer so justly celebrated. By the studies of the great men who succeeded Copernicus, his system had become so perfected as to enable the astronomer to predict, with unerring certainty, the paths of the planets through the heavens. But there was one failing case.

The planet Uranus, then supposed to be the outer planet of the solar system, wandered from the path which theory assigned to it; and although the deviations were but small, yet any discrepancy between theory and observation in so accurate a science as astronomy could not be overlooked. Long before this, the hypothesis had been advanced that the deviations were caused by the attractive force of an unseen and still more distant planet; but, as no such planet had been discovered, the hypothesis had remained until now wholly barren. The hypothesis, however, was reasonable, and furnished the only conceivable explanation of the facts; and, moreover, if true, the received system of astronomy ought to be able to assign the position and magnitude of the disturbing body, the magnitude and direction of the displacements being given.

This possibility was generally appreciated by astronomers, and the very great length and difficulty of the mathematical calculation which

the investigation involved was probably the reason that no one had hitherto undertaken it. Le Verrier, however, had both the courage and the youthful strength required for the work. And now the great work had been done; and, on the 18th of September, Le Verrier had sent to the Observatory of Berlin his communication announcing the final result, namely, that the planet would be found about 5° to the east of the star delta of Capricorn.

The letter containing this announcement was received by Galle, at Berlin, on the 23d, and it was Galle whom we left measuring the position of that faint star on the evening of the 24th. It so happened that a chart of that portion of the heavens had recently been prepared by the Berlin Observatory, and was on the eve of publication; and, on the very evening he received the letter, Galle had found, near the position assigned by Le Verrier, a faint star, which was not marked on this chart. The object differed in appearance from the surrounding stars, but still it was perfectly possible that it might be a fixed star which had escaped previous observation.

But, if a fixed star, its position in the constellation would not vary, while, if a planet, a single night would show a perceptible change of place. Hence, you may conceive of the interest with which Galle was measuring anew its position on the evening of the 24th.

The star had moved, and in the direction which theory indicated; and for once, at least, the world rang with applause at a brilliant scientific conquest, from which there was not one cent of money to be made. Yet, was that conquest any the less important to the world? What had it secured? It had confirmed the theory of astronomy which Copernicus and his successors had built up, and it had clinched the last nail in the proof that those grand conceptions of modern astronomy, now household thoughts, are realities, and not dreams. Certainly no military conquest can compare with this.

Do you smile at the enthusiasm which rates so high a purely intellectual achievement? Go out with me under the heavens, in some starlit night, and, looking up into the depths of space, recall the truths you have learned in regard to that immensity, and allow the imagination free scope as it stretches out into the infinitudes of time, space, and power, carrying the mind on, bound by bound, through the limitless expanse, until even the imagination refuses to follow, and fairly quails before the mighty form of the Infinite, which rises to confront it! Remember now that your forefathers, of only a few centuries back, saw there nothing but a solid dome hemming in the earth and skies, and that you are able to look upon this grand spectacle only because great minds have lived who have opened your intellectual eyes; and then answer me, is not this result worth all the labor, all the sacrifice, all the treasure, it has cost?

Every educated man, who has not sold his birthright for a mess of pottage, lives a grander and a nobler life, because the great astrono-

mers have thought and taught, and this elevation of human life is the greatest achievement of which man can boast. Before it all material conquests appear of little worth, and the lustre of all military or civil glory grows dim. Cherish this intellectual life; foster it; sustain it; do what you can by your own spirit and influence, and, if you are blest with riches, give of your abundance to support and encourage those who, by genius, talent, and devotion, will widen the intellectual kingdom. Be assured you will thus help to confer an inestimable boon on your race and on your country; and the influence for good will not be felt by the *intellectual* life of the nation only; that corruption which is now festering at the heart of our body politic, and threatening its destruction, can in no way be fought and conquered so effectually as by keeping constantly before the nation noble and high ideals; for, where the higher life is cherished and honored, the mercenary and sensual motives of action, which both invite and shield corruption, lose much of their force and power.

But you may tell me that there is a life higher than the intellectual life, and that I have ascribed to science and scholarship influences which come only from a source which I have forgotten, or left out of view. My friends, all truth is one and inseparable, and I have therefore made no distinction in this address between the truths of science and the truths of religion. That grand old word knowledge, as I have used it, includes both, and in just the proportion that you reverence religion, you must reverence also true science. All truth is God's truth, and, in praying for the coming of his kingdom, you certainly do not expect that Nature will be divorced from Grace. If the truths of religion required a special revelation, it must be expected that they would transcend human intelligence. These very conditions imply conflict, but the conflict comes not from the knowledge, but from the ignorance and conceit of men; and the only proper attitude for the devout scholar is 'to labor and to wait.' And what more wonderful confirmation could we have of the essential unity of the two phases of truth than is to be found in the fact that the characteristic of science, which I have been endeavoring to illustrate in this address, is the great prominent feature of Christianity. Christianity was revealed in a life, and ever abides a life in the soul of man, to purify, ennoble, and redeem humanity.

"And so the Word had breath, and wrought,
With human hands, the creed of creeds,
In loveliness of perfect deeds,
More strong than all poetic thought—

"Which he may read that binds the sheaf,
Or builds the house, or digs the grave,
And those wild eyes that watch the wave,
In roarings round the coral-reef."

THE

RADIOMETER:

A FRESH EVIDENCE OF A MOLECULAR UNIVERSE.

BY

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THE RADIOMETER: A FRESH EVIDENCE OF A MOLECULAR UNIVERSE.[1]

NO one who is not familiar with the history of physical science can appreciate how very modern are those grand conceptions which add so much to the loftiness of scientific studies; and of the many who, on one of our starlit nights, look up into the depths of space, and are awed by the thoughts of that immensity which come crowding upon the mind, there are few, I imagine, who realize the fact that almost all the knowledge, which gives such great sublimity to that sight, is the result of comparatively recent scientific investigation; and that the most elementary student can now gain conceptions of the immensity of the universe of which the fathers of astronomy never dreamed. And how very grand are the familiar astronomical facts which the sight of the starry heavens suggests!

Those brilliant points are all suns like the one which forms the centre of our system, and around which our earth revolves; yet so inconceivably remote, that although moving through space with an incredible velocity they have not materially changed their relative position since recorded observations began. Compared with their distance, the distance of our own sun—92,000,000 miles—seems as nothing; yet how inconceivable even that distance is when we endeavor to mete it out with our terrestrial standards! For, if, when Copernicus—the great father of modern astronomy—died, in 1543, just at the close of the Protestant Reformation, a messenger had started for the sun, and traveled ever since with the velocity of a railroad-train—thirty miles an hour—he would not yet have reached his destination!

[1] A lecture delivered in the Sanders Theatre of Harvard University, March 6, 1878.

Evidently, then, no standards, which like our ordinary measures bear a simple or at least a conceivable relation to the dimensions of our own bodies, can help us to stretch a line in such a universe. We must seek for some magnitude which is commensurate with these immensities of space; and, in the wonderfully rapid motion of light, astronomy furnishes us with a suitable standard. By the eclipses of Jupiter's satellites the astronomers have determined that this mysterious effluence reaches us from the sun in eight minutes and a half, and therefore must travel through space with the incredible velocity—shall I dare to name it—of 186,000 miles in a second of time! Yet inconceivably rapid as this motion is, capable of girdling the earth nearly eight times in a single second, the very nearest of the fixed stars, *a* Centauri, is so remote that the light by which it will be seen in the southern heavens to-night, near that magnificent constellation the Southern Cross, must have started on its journey three years and a half ago. But this light comes from merely the threshold of the stellar universe; and the telescope reveals to us stars so distant that, had they been blotted out of existence when history began, the tidings of the event could not yet have reached the earth!

Compare now with these grand conceptions the popular belief of only a few centuries back. Where we look into the infinite depths, our Puritan forefathers saw only a solid dome hemming in the earth and skies, and through whose opened doors the rain descended. They regarded the sun and moon merely as great luminaries set in this firmament to rule the day and night, and to their understandings the stars served no better purpose than the spangles which glitter on the azure ceiling of many a modern church. The great work of Copernicus, "De Orbium Cœlestium Revolutionibus," which was destined, ultimately, to overthrow the crude cosmography which Christianity had inherited from Judaism, was not published until just at the close of the author's life in 1543, the date before mentioned. The telescope, which was required to fully convince the world of its previous error, was not invented until more than half a century later, and it was not until 1835 that Struve detected the parallax of *a* Lyræ. The measurement of this parallax, together with Bessel's determination of the parallax of 61 Cygni, and Henderson's that of *a* Centauri, at about the same time, gave us our first accurate knowledge of the distances of the fixed stars.

To the thought I have endeavored to express I must add another, before I can draw the lesson which I wish to teach. Great scientific truths become popularized very slowly, and, after they have been thoroughly worked out by the investigators, it is often many years before they become a part of the current knowledge of mankind. It was fully a century after Copernicus died, with his great volume—still wet from the press of Nuremburg—in his hands, before the Copernican theory was generally accepted even by the learned; and the intolerant spirit with which this work was received, and the persecution which

Galileo encountered more than half a century later, were due solely to the circumstance that the new theory tended to subvert the popular faith in the cosmography of the Church. In modern times, with the many popular expositors of science, the diffusion of new truth is more rapid; but even now there is always a long interval after any great discovery in abstract science before the new conception is translated into the language of common life, so that it can be apprehended by the mass even of educated men.

I have thus dwelt on what must be familiar facts in the past history of astronomy, because they illustrate and will help you to realize the present condition of a much younger branch of physical science: for in the transition-period I have described there exists now a conception which opens a vision into the microcosmos beneath us as extensive and as grand as that which the Copernican theory revealed into the macrocosmos above us.

The conception to which I refer will be at once suggested to every scientific scholar by the word *molecule.* This word is a Latin diminutive, which means, primarily, a small mass of matter; and although heretofore often applied in mechanics to the indefinitely small particles of a body between which the attractive or repulsive forces might be supposed to act, it has only recently acquired the exact significance with which we now use it.

In attempting to discover the original usage of the word molecule, I was surprised to find that it was apparently first introduced into science by the great French naturalist, Buffon, who employed the term in a very peculiar sense. Buffon does not seem to have been troubled with the problem which so engrosses our modern naturalists—how the vegetable and animal kingdoms were developed into their present condition—but he was greatly exercised by an equally difficult problem, which seems to have been lost sight of in the present controversy, and which is just as obscure to-day as it was in Buffon's time, at the close of the last century, and that is, Why species are so persistent in Nature; why the acorn *always* grows into the oak, and why every creature *always* produces of its kind. And, if you will reflect upon it, I am sure you will conclude that this last is by far the more fundamental problem of the two, and one which necessarily includes the first. That of two eggs, in which no anatomist can discover any structural difference, the one should, in a few short years, *develop* an intelligence like Newton's, while the other soon ends in a Guinea-pig, is certainly a greater mystery than that, in the course of unnumbered ages, monkeys, by insensible gradations, should *grow* into men.

In order to explain the remarkable constancy of species, Buffon advanced a theory which, when freed from a good deal that was fanciful, may be expressed thus: The attributes of every species, whether of plants or of animals, reside in their ultimate particles, or, to use a more philosophical but less familiar word, *inhere* in these particles, which

Buffon names *organic molecules.* According to Buffon, the oak owes all the peculiarities of its organization to the special oak-molecules of which it consists ; and so all the differences in the vegetable or animal kingdom, from the lowest to the highest species, depend on fundamental peculiarities with which their respective molecules were primarily endowed. There must, of course, be as many kinds of molecules as there are different species of living beings ; but, while the molecules of the same species were supposed to be exactly alike and to have a strong affinity or attraction for each other, those of different species were assumed to be inherently distinct and to have no such affinities. Buffon further assumed that these molecules of organic Nature were diffused more or less widely through the atmosphere and through the soil, and that the acorn grew to the oak simply because, consisting itself of oak-molecules, it could draw only oak-molecules from the surrounding media.

With our present knowledge of the chemical constitution of organic beings, we can find a great deal that is both fantastic and absurd in this theory of Buffon, but it must be remembered that the science of chemistry is almost wholly a growth of the present century, while Buffon died in 1788 ; and, if we look at the theory solely from the standpoint of his knowledge, we shall find in it much that was worthy of this great man. Indeed, in our time the essential features of the theory of Buffon have been transferred from natural history to chemistry almost unchanged.

According to our modern chemistry, the qualities of every substance reside or inhere in its molecules. Take this lump of sugar. It has certain qualities with which every one is familiar. Are those qualities attributes of the lump or of its parts ? Certainly of its parts. For, if we break up the lump, the smallest particles will still taste sweet and show all the characteristics of sugar. Could we then carry on this subdivision indefinitely provided only we had senses or tests delicate enough to recognize the qualities of sugar in the resulting particles ? To this question, modern chemistry answers decidedly : No ! You would before long reach the smallest mass that can have the qualities of sugar. You would have no difficulty in breaking up these masses, but you would then obtain not smaller particles of sugar, but particles of those utterly different substances which we call carbon, oxygen, and hydrogen, in a word particles of the elementary substances of which sugar consists. These ultimate particles of sugar we call the molecules of sugar, and thus we come to the present chemical definition of a molecule, " *The smallest particles of a substance in which its qualities inhere,*" which, as you see, is a reproduction of Buffon's idea, although applied to matter and not to organism.

A lump of sugar, then, has its peculiar qualities because it is an aggregate of molecules which have those qualities, and a lump of salt differs from a lump of sugar simply because the molecules of salt differ

from those of sugar, and so with every other substance. There are as many kinds of molecules in Nature as there are different substances, but all the molecules of the same substance are absolutely alike in every respect.

Thus far, as you see, we are merely reviving in a different association the old ideas of Buffon. But just at this point comes in a new conception, which gives far greater grandeur to our modern theory: for we conceive that those smallest particles in which the qualities of a substance inhere are definite bodies or systems of bodies moving in space, and that *a lump of sugar is a universe of moving worlds.*

If on a clear night you direct a telescope to one of the many star-clusters of our northern heavens, you will have presented to the eye as good a diagram as we can at present draw of what we suppose would, under certain circumstances, be seen in a lump of sugar if we could look into the molecular universe with the same facility with which the telescope penetrates the depths of space. Do you tell me that the absurdities of Buffon were wisdom when compared with such wild speculations as these? The criticism is simply what I expected, and I must remind you that, as I intimated at the outset, this conception of modern science is in the transition period of which I then spoke, and, although very familiar to scientific scholars, has not yet been grasped by the popular mind. I can, further, only add that, wild as it may appear, the idea is the growth of legitimate scientific investigation, and express my conviction that it will soon become as much a part of the popular belief as those grand conceptions of astronomy to which I have referred. Do you rejoin that we can see the suns in a stellar cluster, but cannot even begin to see the molecules? I must again remind you that, in fact, you only see points of light in the field of the telescope, and that your knowledge that these points are immensely distant suns is an inference of astronomical science; and further that our knowledge—if I may so call our confident belief—that the lump of sugar is an aggregate of moving molecules is an equally legitimate inference of molecular mechanics, a science which, although so much newer, is as positive a field of study as astronomy. Moreover, sight is not the only avenue to knowledge; and, although our material limitations forbid us to expect that the microscope will ever be able to penetrate the molecular universe, yet we feel assured that we have been able by strictly experimental methods to weigh molecular masses, and measure molecular magnitudes, with as much accuracy as those of the fixed stars.

Of all forms of matter the gas has the simplest molecular structure, and, as might be anticipated, our knowledge of molecular magnitudes is as yet chiefly confined to materials of this class. I have given below some of the results which have been obtained in regard to the molecular magnitudes of hydrogen gas, one of the best studied of this class of substances; and, although the vast numbers are as inconceivable as are those of astronomy, they cannot fail to impress you with the reality of

the magnitudes they represent. I take hydrogen gas for my illustration rather than air, because our atmosphere is a mixture of two gases, oxygen and nitrogen, and therefore its condition is less simple than that of a perfectly homogeneous material like hydrogen. The molecular dimensions of other substances, although varying very greatly in their relative values, are of the same order as these.[1]

Dimensions of Hydrogen Molecules calculated for Temperature of Melting Ice and for the Mean Height of the Barometer at the Sea-Level.

Mean velocity, 6,099 feet a second.
Mean path, 31 ten-millionths of an inch.
Collisions, 17,750 millions each second.
Diameter, 438,000, side by side, measure $\frac{1}{100}$ of an inch.
Mass, 14 (millions^3) weigh $\frac{1}{1000}$ of a grain.
Gas-volume, 311 (millions^3) fill one cubic inch.

To explain how the values here presented were obtained would be out of place in a popular lecture,[2] but a few words in regard to two or three of the data are required to elucidate the subject of this lecture.

First, then, in regard to the mass or weight of the molecules. So far as their relative values are concerned, chemistry gives us the means of determining the molecular weights with very great accuracy; but when we attempt to estimate their weights in fractions of a grain—the smallest of our common standards—we cannot expect precision, simply because the magnitudes compared are of such a different order; and the same is true of most of the other absolute dimensions, such as the diameter and volume of the molecules. We only regard the values given in our table as a very rough estimate, but still we have good

[1] As some of the readers of this journal may be interested to compare these values, we reproduce the "Table of Molecular Data" from Prof. Clerk Maxwell's lecture on "Molecules," delivered before the British Association at Bradford, and published in *Nature*, September 25, 1873.

Molecular Magnitudes at Standard Temperature and Pressure, 0° *C. and* 76 *c. m.*

RANK ACCORDING TO ACCURACY OF KNOWLEDGE.	Hydrogen.	Oxygen.	Carbonic Oxide.	Carbonic Dioxide.
RANK I.				
Relative mass	1	16	14	22
Velocity in metres per second	1,859	465	497	396
RANK II.				
Mean path in ten billionths ($_{10}-^{10}$) of a metre	965	560	482	379
Collisions each second—number of millions	17,750	7,646	9,489	9,720
RANK III.				
Diameter in hundred billionths ($_{10}-^{11}$) of a metre	58	76	83	93
Mass in ten million million million millionths ($_{10}-^{25}$) of a gramme	46	736	644	1,012

Number of molecules in one cubic centimetre of every gas is nineteen million million million on 19 ($_{10}{}^{18}$).

Two million hydrogen molecules side by side measure a little over one millimetre.

[2] *See* Prof. Maxwell's lecture, *loc. cit.;* also Appletons' "Cyclopædia," article "Molecules."

grounds for believing that they are sufficiently accurate to give us a true idea of the order of the quantities with which we are dealing; and it will be seen that although the numbers required to express the relations to our ordinary standards are so large, these molecular magnitudes are no more removed from us on the one side than are those of astronomy on the other.

Passing next to the velocity of the molecular motion, we find in that a quantity which, although large, is commensurate with the velocity of sound, the velocity of a rifle-ball, and the velocities of many other motions with which we are familiar. We are, therefore, not comparing, as before, quantities of an utterly different order, and we have confidence that we have been able to determine the value within very narrow limits of error. But how surprising the result is! Those molecules of hydrogen are constantly moving to and fro with this great velocity, and not only are the molecules of all aëriform substances moving at similar, although differing, rates, but the same is equally true of the molecules of every substance, whatever may be its state of aggregation.

The gas is the simplest molecular condition of matter, because in this state the molecules are so far separated from each other that their motions are not influenced by mutual attractions. Hence, in accordance with the well-known laws of motion, gas-molecules must always move in straight lines and with a constant velocity until they collide with each other or strike against the walls of the containing vessel, when, in consequence of their elasticity, they at once rebound and start on a new path with a new velocity. In these collisions, however, there is no loss of motion, for, as the molecules have the same weight, and are perfectly elastic, they simply change velocities, and whatever one may lose the other must gain.

But if the velocity changes in this way, you may ask, What meaning has the definite value given in our table? The answer is, that this is the mean value of the velocity of all the molecules in a mass of hydrogen gas under the assumed conditions; and, by the principle just stated, the mean value cannot be changed by the collisions of the molecules among themselves, however great may be the change in the motion of the individuals.

In both liquids and solids the molecular motions are undoubtedly as active as in a gas, but they must be greatly influenced by the mutual attractions which hold the particles together, and hence the conditions are far more complicated, and present a problem which we have been able to solve only very imperfectly, and with which, fortunately, we have not at present to deal.

Limiting, then, our study to the molecular condition of a gas, picture to yourselves what must be the condition of our atmosphere, with its molecules flying about in all directions. Conceive what a molecular storm must be, raging about us, and how it must beat against our bodies and against every exposed surface. The molecules of our

atmosphere move, on an average, nearly four (3.8) times slower than those of hydrogen under the same conditions; but then they weigh, on an average, fourteen and a half times more than hydrogen-molecules, and therefore strike with as great energy. And do not think that the effect of these blows is insignificant because the molecular projectiles are so small; they make up by their number for what they want in size.

Consider, for example, a cubic yard of air, which, if measured at the freezing-point, weighs considerably over two pounds. That cubic yard of material contains over two pounds of molecules, which are moving with an average velocity of 1,605 feet a second, and this motion is equivalent, in every respect, to that of a cannon-ball of equal weight, rushing along its path at the same tremendous rate. Of course, this is true of every cubic yard of air at the same temperature; and, if the motion of the molecules of the atmosphere around us could by any means be turned into one and the same direction, the result would be a hurricane sweeping over the earth with this velocity—that is, at the rate of 1,094 miles an hour—whose destructive violence not even the Pyramids could withstand.

Living as we do in the midst of a molecular tornado capable of such effects, our safety lies wholly in the circumstance that the storm beats equally in all directions at the same time, and the force is thus so exactly balanced that we are wholly unconscious of the tumult. Not even the aspen-leaf is stirred, nor the most delicate membrane broken; but let us remove the air from one of the surfaces of such a membrane, and then the power of the molecular storm becomes evident, as in the familiar experiments with an air-pump.

As has already been intimated, the values of the velocities both of hydrogen and of air molecules given above were measured at a definite temperature, 32° of our Fahrenheit thermometer, the freezing-point of water; and this introduces a very important point bearing on our subject, namely, that the molecular velocities vary very greatly with the temperature. Indeed, according to our theory, this very molecular motion constitutes that state or condition of matter which we call temperature. A hot body is one whose molecules are moving comparatively rapidly, and a cold body one in which they are moving comparatively slowly. Without, however, entering into further details, which would involve the whole mechanical theory of heat, let me call your attention to a single consequence of the principle I have stated.

When we heat hydrogen, air, or any mass of gas, we simply increase the velocity of its moving molecules. When we cool the gas, we simply lessen the velocity of the same molecules. Take a current of air which enters a room through a furnace. In passing it comes in contact with heated iron, and, as we say, is heated. But, as we view the process, the molecules of the air, while in contact with the hot iron, collide with the very rapidly-oscillating metallic molecules, and fly back as a billiard-ball would under similar circumstances, with a greatly-in-

creased velocity, and it is this more rapid motion which alone constitutes the higher temperature.

Consider, next, what must be the effect on the surface. A moment's reflection will show that the normal pressure exerted by the molecular storm, always raging in the atmosphere, is due not only to the impact of the molecules, but also to the reaction caused by their rebound. When the molecules rebound they are, as it were, driven away from the surface in virtue of the inherent elasticity both of the surface and of the molecules. Now, what takes place when one mass of matter is driven away from another—when a cannon-ball is driven out of a gun, for example? Why, the gun *kicks!* And so every surface from which molecules rebound must *kick;* and, if the velocity is not changed by the collision, one-half of the pressure caused by the molecular bombardment is due to the recoil. From a heated surface, as we have said, the molecules rebound with an increased velocity, and hence the recoil must be proportionally increased, determining a greater pressure against the surface.

According to this theory, then, we should expect that the air would press unequally against surfaces at different temperatures, and that, other things being equal, the pressure exerted would be greater the higher the temperature of the surface. Such a result, of course, is wholly contrary to common experience, which tells us that a uniform mass of air presses equally in all directions and against all surfaces of the same area, whatever may be their condition. It would seem, then, at first sight, as if we had here met with a conspicuous case in which our theory fails. But further study will convince us that the result is just what we should expect in a dense atmosphere like that in which we dwell; and, in order that this may become evident, let me next call your attention to another class of molecular magnitudes.

It must seem strange indeed that we should be able to measure molecular velocities, but the next point I have to bring to your notice is stranger yet, for we are confident that we have been able to determine with approximate accuracy for each kind of gas-molecule the average number of times one of these little bodies runs against its neighbors in a second, assuming, of course, that the conditions of the gas are given. Knowing, now, the molecular velocity and the number of collisions a second, we can readily calculate the mean path of the molecule—that is, the average distance it moves, under the same conditions, between two successive collisions. Of course, for any one molecule, this path must be constantly varying; since, while at one time the molecule may find a clear coast and make a long run, the very next time it may hardly start before its course is arrested. Still, taking a mass of gas under constant conditions, the doctrine of averages shows that the mean path must have a definite value, and an illustration will give an idea of the manner in which we have been able to estimate it.

The nauseous smelling gas we call sulphide of hydrogen has a density only a little greater than that of air, and its molecules must therefore move with very nearly as great velocity as the average air-molecule—that is to say, about 1,480 feet a second; and we might therefore expect that, on opening a jar of the gas, its molecules would spread instantly through the surrounding atmosphere. But so far from this, if the air is quiet, so that the gas is not transported by currents, a very considerable time will elapse before the characteristic odor is perceived on the opposite side of an ordinary room. The reason is obvious —the molecules must elbow their way through the crowd of air-molecules which already occupy the space, and can therefore advance only slowly; and it is obvious that, the oftener they come into collision with their neighbors, the slower their progress must be. Knowing, then, the mean velocity of the molecular motion, and being able to measure by appropriate means *the rate of diffusion*, as it is called, we have the data from which we can calculate both the number of collisions in a second and also the mean path between two successive collisions. The results, as we must expect, are of the same order as the other molecular magnitudes. But inconceivably short as the free[1] path of a molecule certainly is, it is still, in the case of hydrogen gas, 136 times the diameter of the moving body, which would certainly be regarded among men as quite ample elbow-room.

Although, in this lecture, I have as yet had no occasion to mention the radiometer, I have by no means forgotten my main subject, and everything which has been said has had a direct bearing on the theory of this remarkable instrument; and still, before you can understand the great interest with which it is regarded, we must follow out another line of thought, converging on the same point.

One of the most remarkable results of modern science is the discovery that all energy at work on the surface of this planet comes from the sun. Most of you probably saw, at our Centennial Exhibition, that great artificial cascade in Machinery Hall, and were impressed with the power of the steam-pump which could keep flowing such a mass of water. But, also, when you stood before the falls at Niagara, did you realize the fact that the enormous floods of water, which you saw surging over those cliffs, were in like manner supplied by an all-powerful pump, and that pump the sun? And not only is this true, but it is equally true that every drop of water that falls, every wave that beats, every wind that blows, every creature that moves on the surface of the earth, one and all, are animated by that mysterious effluence we call the sunbeam. I say mysterious effluence; for how that power is trans-

[1] There is an obvious distinction between the free and the disturbed path of a molecule, and we cannot overlook in our calculations the perturbations which the collisions necessarily entail. Such considerations greatly complicate the problem, which is far more difficult than would appear from the superficial view of the subject that can alone be given in a popular lecture.

mitted over those 92,000,000 miles between the earth and the sun, is still one of the greatest mysteries of Nature.

In the science of optics, as is well known, the phenomena of light are explained by the assumption that the energy is transmitted in waves through a medium which fills all space, called the luminiferous ether, and there is no question that this theory of Nature, known in science as the Undulatory Theory of Light, is, as a working hypothesis, one of the most comprehensive and searching which the human mind has ever framed. It has both correlated known facts and pointed the way to remarkable discoveries. But, the moment we attempt to apply it to the problem before us, it demands conditions which tax even a philosopher's credulity.

As sad experience on the ocean only too frequently teaches, energy can be transmitted by waves as well as in any other way. But every mechanic will tell you that the transmission of energy, whatever be the means employed, implies certain well-known conditions. Let it be that the energy is to be used to turn the spindles of a cotton-mill. The engineer can tell you just how many horse-power he must supply for every working-day, and it is equally true that a definite amount of energy must come from the sun to do each day's work on the surface of the globe. Further, the engineer will also tell you that, in order to transmit the power from his turbine or his steam-engine, he must have shafts and pulleys and belts of adequate strength, and he knows in every case what is the lowest limit of safety. In like manner, the medium through which the energy which runs the world is transmitted must be strong enough to do the immense work put upon it; and, if the energy is transmitted by waves, this implies that the medium must have an enormously great elasticity, an elasticity vastly greater than that of the best-tempered steel.

But turn now to the astronomers, and learn what they have to tell us in regard to the assumed luminiferous ether through which all this energy is supposed to be transmitted. Our planet is rushing in its orbit around the sun at an average rate of over 1,000 miles a minute, and makes its annual journey of some 550,000,000 miles in 365 days 6 hours 9 seconds and $\frac{6}{10}$ of a second. Mark the tenths; for astronomical observations are so accurate that, if the length of the year varied permanently by the tenth of a second, we should know it; and you can readily understand that, if there were a medium in space which offered as much resistance to the motion of the earth as would gossamer threads to a race-horse, the planet could never come up to time, year after year, to the tenth of a second.

How, then, can we save our theory, by which we set so much, and rightly, because it has helped us so effectively in studying Nature? If we may be allowed such an extravagant solecism, let us suppose that the engineer of our previous illustration was the hero of a fairy-tale. He has built a mill, set a steam-engine in the basement, arranged his

spindles above, and is connecting the pulleys by the usual belts, when some stern necessity requires him to transmit all the energy with cobwebs. Of course, a good fairy comes to his aid, and what does she do? Simply makes the cobwebs indefinitely strong. So the physicists, not to be outdone by any fairies, make their ether indefinitely elastic, and their theory lands them just here, with a medium filling all space, thousands of times more elastic than steel, and thousands on thousands of times less dense than hydrogen gas. There must be a fallacy somewhere, and I strongly suspect it is to be found in our ordinary materialistic notions of causation, which involve the old metaphysical dogma, "*nulla actio in distans*," and which in our day have culminated in the famous apothegm of the German materialist, "Kein Phosphor kein Gedanke."

But it is not my purpose to discuss the doctrines of causation, and I have dwelt on the difficulty, which this subject presents in connection with the undulatory theory, solely because I wished you to appreciate the great interest with which scientific men have looked for some direct manifestation of the mechanical action of light. It is true that the ether-waves must have dimensions similar to those of the molecules discussed above, and we must expect, therefore, that they would act primarily on the molecules and not on masses of matter. But still the well-known principles of wave-motion have led competent physicists to maintain that a more or less considerable pressure ought to be exerted by the ether-waves on the surfaces against which they beat, as a partial resultant of the molecular tremors first imparted. Already, in the last century, attempts were made to discover some evidence of such action, and in various experiments the sun's direct rays were concentrated on films, delicately suspended and carefully protected from all other extraneous influences, but without any apparent effect; and thus the question remained until about three years ago, when the scientific world were startled by the announcement of Mr. Crookes, of London, that, on suspending a small piece of blackened alder-pith in the very perfect vacuum which can now be obtained with the mercury-pump, invented by Sprengel, he had seen this light body actually repelled by the sun's rays; and they were still more startled, when, after a few further experiments, he presented us with the instrument he called a radiometer, in which the sun's rays do the no inconsiderable work of turning a small wheel. Let us examine for a moment the construction of this remarkable instrument.

The moving part of the radiometer is a small horizontal wheel, to the ends of whose arms are fastened vertical vanes, usually of mica, and blackened on one side. A glass cap forms the hub, and by the glass-blower's art the wheel is inclosed in a glass bulb, so that the cap rests on the point of a cambric needle; and the wheel is so delicately balanced on this pivot that it turns with the greatest freedom. From the interior of the bulb the air is now exhausted by means of the Sprengel pump, until less than $\frac{1}{1000}$ of the original quantity is left,

and the only opening is then hermetically sealed. If, now, the sun's light or even the light from a candle shines on the vanes, the blackened surfaces—which are coated with lamp-black—are repelled, and, these being symmetrically placed around the wheel, the several forces conspire to produce the rapid motion which results. The effect has all the appearance of a direct mechanical action exerted by the light, and for some time was so regarded by Mr. Crookes and other eminent physicists, although in his published papers it should be added that Mr. Crookes carefully abstained from speculating on the subject—aiming, as he has since said, to keep himself unbiased by any theory, while he accumulated the facts upon which a satisfactory explanation might be based.

Singularly, however, the first aspect of the new phenomena proved to be wholly deceptive; and the motion, so far from being an effect of the direct mechanical action of the waves of light, is now believed to be a new and very striking manifestation of molecular motion. To this opinion Mr. Crookes himself has come, and in a recent article he writes: "Twelve months' research, however, has thrown much light on these actions; and the explanation afforded by the dynamical theory of gases makes, what was a year ago obscure and contradictory, now reasonable and intelligible."

As is frequently the case in Nature, the chief effect is here obscured by various subordinate phenomena, and it is not surprising that a great difference of opinion should have arisen in regard to the cause of the motion. This would not be an appropriate place to describe the numerous investigations occasioned by the controversy, many of which show in a most striking manner how easily experimental evidence may be honestly misinterpreted in support of a preconceived opinion. I will, however, venture to trespass further on your patience, so far as to describe the few experiments by which very early in the controversy I satisfied my own mind on the subject.

When two years ago I had for the first time an opportunity of experimenting with a radiometer, the opinion was still prevalent that the motion of the wheel was a direct mechanical effect of the waves of light, and therefore that the impulses came from the outside of the instrument, the waves passing freely through the glass envelope. At the outset this opinion did not seem to me to be reasonable, or in harmony with well-known facts; for, knowing how great must be the molecular disturbance caused by the sun's rays as shown by their heating power, I could not believe that a residual action, such as has been referred to, would first appear in these delicate phenomena observed by Mr. Crookes, and should only be manifested in the vacuum of a mercury-pump.

On examining the instrument, my attention was at once arrested by the lampblack coating on the alternate surfaces of the vanes; and from the remarkable power of lampblack to absorb radiant heat it was

evident at once that, whatever other effects the rays from the sun or from a flame might cause, they must necessarily determine a constant difference of temperature between the two surfaces of the vanes; and the thought at once occurred that, after all, the motion might be a direct result of this difference of temperature—in other words, that the radiometer might be a small heat-engine, whose motions, like those of every other heat-engine, depend on the difference of temperature between its parts.

But, if this were true, the effect ought to be proportional solely to the heating power of the rays, and a very easy means of roughly testing this question was at hand. It is well known that an aqueous solution of alum, although transmitting light as freely as the purest water, powerfully absorbs those rays, of any source, which have the chief heating power. Accordingly, I interposed what we call an alum-cell in the path of the rays shining on the radiometer, when, although the light on the vanes was as bright as before, the motion was almost completely arrested.

This experiment, however, was not conclusive, as it might still be said that the *heat*-giving rays acted *mechanically;* and it must be admitted that the chief part of the energy in the rays, even from the most brilliant luminous sources, always takes the form of heat. But, if the action is mechanical, the reaction must be against the medium through which the rays are transmitted, while, if the radiometer is simply a heat-engine, the action and reaction must be, ultimately at least, between the heater and the cooler, which in this case are respectively the blackened surfaces of the vanes and the glass walls of the inclosing bulb; and here, again, a very easy methcd of testing the actual condition at once suggested itself.

If the motion of the radiometer-wheel is an effect of mechanical impulses transmitted in the direction of the beam of light, it was certainly to be expected that the beam would act on the lustrous as well as on the blackened mica surfaces, however large might be the difference in the resultants producing mechanical motion in consequence of the great absorbing power of the lampblack. Moreover, since the instrument is so constructed that of two vanes, on opposite sides of the wheel, one always presents a blackened and the other a lustrous surface to an incident beam, we should further expect to find in the motion of the wheel a differential phenomenon, due to the unequal action of the light on these surfaces. On the other hand, if the radiometer is a heat-engine, and the reaction takes place between the heated blackened surfaces of the vanes and the colder glass, it is evident that the total effect will be simply the sum of the effects at the several surfaces.

In order to investigate the question thus presented, I placed the radiometer before a common kerosene-lamp, and observed, with a stop-watch, the number of seconds elapsed during ten revolutions of the little wheel. Finding that this number was absolutely constant, I next

screened one-half of the bulb, so that only the blackened faces were exposed to the light as the wheel turned them into the beam. Again, I several times observed the number of seconds during ten turns, which, although equally constant, was greater than before. Lastly, I screened the blackened surfaces so that, as the wheel turned, only the lustrous surfaces of mica were exposed to the light, when, to my surprise, the wheel continued to turn in the same direction as before, although much more slowly. It appeared as if the lustrous surfaces were attracted by the light. Again I observed the time of ten revolutions, and here I have collected my results, reducing them, in the last column, so as to show the corresponding number of revolutions in the same time:

CONDITIONS.	Time of Ten Revolutions.	No. of Revolutions in same Time.
Both faces exposed...........................	8 seconds.	319
Blackened faces only.......................	11 "	232
Mica faces only................................	29 "	88

It will be noticed that 88 + 232 equals very nearly 319. Evidently the effect, so far from being differential, is concurrent. Hence, the action which causes the motion must take place between the parts of the instrument, and cannot be a direct effect of impulses imparted by ether-waves; or else we are driven to the most improbable alternative, that lampblack and mica should have such a remarkable selective power that the impulses imparted by the light should exert a repulsive force at one surface and an attractive force at the other. Were there, however, such an improbable effect, it must be independent of the thickness of the mica vanes; while on the other hand, if, as seemed to us now most probable, the whole effect depended on the difference of temperature between the lampblack and the mica, and if the light produced an effect on the mica surface only because, the mica plate being diathermous to a very considerable extent, the lampblack became heated through the plate more than the plate itself, then it would follow that, if we used a thicker mica plate, which would absorb more of the heat, we ought to obtain a marked difference of effect. Accordingly, we repeated the experiment with an equally sensitive radiometer, which we made for the purpose, with comparatively thick vanes, and with this the effect of a beam of light on the mica surface was absolutely null, the wheel revolving in the same time, whether these faces were protected or not.

But one thing was now wanting to make the demonstration complete. A heat-engine is reversible, and if the motion of the radiometer depended on the circumstance that the temperature of the blackened faces of the vanes was higher than that of the glass, then by reversing the conditions we ought to reverse the motion. Accordingly, I carefully heated the glass bulb over a lamp, until it was as hot as the hand

would bear, and then placed the instrument in a cold room, trusting to the great radiating power of lampblack to maintain the temperature of the blackened surfaces of the vanes below that of the glass. Immediately the wheel began to turn in the opposite direction, and continued to turn until the temperature of the glass came into equilibrium with the surrounding objects.

These early experiments have since been confirmed to the fullest extent, and no physicist at the present day can reasonably doubt that the radiometer is a very beautiful example of a heat-engine, and it is the first that has been made to work continuously by the heat of the sunbeam. But it is one thing to show that the instrument is a heat-engine, and quite another thing to explain in detail the manner in which it acts. In regard to the last point, there is still room for much difference of opinion, although physicists are generally agreed in referring the action to the residual gas that is left in the bulb. As for myself, I became strongly persuaded—after experimenting with more than one hundred of these instruments, made under my own eye, with every variation of conditions I could suggest—*that the effect was due to the same cause which determines gas-pressure*, and, according to the dynamical theory of gases, this amounts to saying that the effect is due to molecular motion. I have not time, however, to describe either my own experiments on which this opinion was first based, or the far more thorough investigations since made by others, which have served to strengthen the first impression.[1] But, after our previous discussions, a few words will suffice to show how the molecular theory explains the new phenomena.

Although the air in the bulb has been so nearly exhausted that less than the one-thousandth part remains, yet it must be borne in mind that the number of molecules left behind is by no means inconsiderable. As will be seen by referring to our table, there must still be no less than 311,000 million million in every cubic inch. Moreover, the absolute pressure which this residual gas exerts is a very appreciable quantity. It is simply the one-thousandth of the normal pressure of the atmosphere, that is, of $14\frac{7}{10}$ pounds on a square inch; which is equivalent to a little over 100 grains on the same area. Now, the area of the blackened surfaces of the vanes of an ordinary radiometer measures just about a square inch, and the wheel is mounted so delicately that a constant pressure of one-tenth of a grain would be sufficient to produce rapid motion. So that a difference of pressure on the opposite faces of the vanes, equal to one one-thousandth of the whole amount, is all that we need account for; and, as can easily be calculated, a difference of temperature of less than half a degree Fahrenheit would cause all this difference in the pressure of the rarefied air.

But you may ask, How can such a difference of pressure exist on

[1] *See* notice of these investigations by the author of this article, in *American Journal of Science and Arts*, September, 1877 (3), xiv., 231.

different surfaces exposed to one and the same medium? and your question is a perfectly legitimate one; for it is just here that the new phenomena seem to belie all our previous experience. If, however, you followed me in my very partial exposition of the mechanical theory of gases, you will easily see that on this theory it is a more difficult question to explain why such a difference of pressure does not manifest itself in every gas medium and under all conditions between any two surfaces having different temperatures.

We saw that gas-pressure is a double effect, caused both by the impact of molecules and by the recoil of the surface attending their rebound. We also saw that when molecules strike a heated surface they rebound with increased velocity, and hence produce an increased pressure against the surface, the greater the higher the temperature. According to this theory, then, we should expect to find the same atmosphere pressing unequally on equal surfaces if at different temperatures; and the difference in the pressure on the lampblack and mica surfaces of the vanes, which the motion of the radiometer-wheel necessarily implies, is therefore simply the normal effect of the mechanical condition of every gas medium. The real difficulty is, to explain why we must exhaust the air so perfectly before the effect manifests itself.

The new theory is equal to the emergency. As has been already pointed out, in the ordinary state of the air the amplitude of the molecular motion is exceedingly small, not over a few ten-millionths of an inch—a very small fraction, therefore, of the height of the inequalities on the lampblack surfaces of the vanes of a radiometer. Under such circumstances, evidently the molecules would not leave the heated surface, but simply bound back and forth between the vanes and the surrounding mass of dense air, which, being almost absolutely a non-conductor of heat, must act essentially like an elastic solid wall confining the vanes on either side. For the time being, and until replaced by convection-currents, the oscillating molecules are as much a part of the vanes as our atmosphere is a part of the earth; and on this system, as a whole, the homogeneous dense air which surrounds it must press equally from all directions. In proportion, however, as the air is exhausted, the molecules find more room and the amplitude of the molecular motion is increased, and when a very high degree of exhaustion is reached the air-particles no longer bound back and forth on the vanes without change of condition, but they either bound off entirely like a ball from a cannon, or else, having transferred a portion of their momentum, return with diminished velocity, and in either case the force of the reaction is felt.[1]

[1] The reader will, of course, distinguish between the differential action on the opposite faces of the vanes of the radiometer and the reaction between the vanes and the glass which are the heater and the cooler of the little engine. Nor will it be necessary to remind any student that a popular view of such a complex subject must be necessarily partial. In the present case we not only meet with the usual difficulties in this respect, but,

Thus it appears that we have been able to show by very definite experimental evidence that the radiometer is a heat-engine. We have also been able to show that such a difference of temperature as the radiation must produce in the air in *direct* contact with the opposite faces of the vanes of the radiometer would determine a difference of tension, which is sufficient to account for the motion of the wheel. Finally, we have shown, as fully as is possible in a popular lecture, that, according to the mechanical theory of gases, such a difference of tension would have its normal effect only in a highly-rarefied atmosphere, and thus we have brought the new phenomena into harmony with the general principles of molecular mechanics previously established.

More than this cannot be said of the steam-engine, although, of course, in the older engine the measurements on which the theory is based are vastly more accurate and complete. But the moment we attempt to go beyond the general principles of heat-engines, of which the steam-engine is such a conspicuous illustration, and explain how the heat is transformed into motion, we have to resort to the molecular theory just as in the case of the radiometer; and the motion of the steam-engine seems to us less wonderful than that of the radiometer, only because it is more familiar and more completely harmonized with the rest of our knowledge. Moreover, the very molecular theory which we call upon to explain the steam-engine involves consequences which, as we have seen, have been first realized in the radiometer; and thus it

moreover, the principles of molecular mechanics have not been so fully developed as to preclude important differences of opinion between equally competent authorities in regard to the details of the theory. To avoid misapprehension, we may here add that, in order to obtain in the radiometer a reaction between the heater and the cooler, it is not necessary that the space between them should actually be crossed by the moving molecules. It is only necessary that the momentum should be transferred across the space, and this may take place along lines consisting of many molecules each. The theory, however, shows that such a transfer can only take place in a highly-rarefied medium. In an atmosphere of ordinary density, the accession of heat which the vanes of a radiometer might receive from a radiant source would be diffused through the mass of the inclosed air. This amounts to saying that the momentum would be so diffused, and hence, under such circumstances, the molecular motion would not determine any reaction between the vanes and the glass envelope. Indeed, a dense mass of gas presents to the conduction of heat, which represents momentum, a wall far more impenetrable than the surrounding glass, and the diffusion of heat is almost wholly brought about by convection-currents which rise from the heated surfaces. It will thus be seen that the great non-conducting power of air comes into play to prevent not only the transfer of momentum from the vanes to the glass, but also, almost entirely, any direct transfer to the surrounding mass of gas. Hence, as stated above, the heated molecules bound back and forth on the vanes without change of condition, and the mass of the air retains its uniform tension in all parts of the bulb, except in so far as this is slowly altered by the convection-currents just referred to. As the atmosphere, however, becomes less dense, the diffusion of heat by convection diminishes, and that by molecular motion (conduction) increases until the last greatly predominates. When, now, the exhaustion reaches so great a degree that the heat, or momentum, is rapidly transferred from the heater to the cooler by an exaggeration, or, possibly, a modification of the mode of action we call conduction, then we have the reaction on which the motion of the radiometer-wheel depends.

is that this new instrument, although disappointing the first expectations of its discoverer, has furnished a very striking confirmation of this wonderful theory. Indeed, the confirmation is so remote and yet so close, so unexpected and yet so strong, that the new phenomena lmost seem to be a direct manifestation of the molecular motion which our theory assumes ; and when a new discovery thus confirms the accuracy of a previous generalization, and gives us additional reason to believe that the glimpses we have gained into the order of Nature are trustworthy, it excites, with reason, among scientific scholars the warmest interest.

And when we consider the vast scope of the molecular theory, the order on order of existences which it opens to the imagination, how can we fail to be impressed with the position in which it places man midway between the molecular cosmos on the one side and the stellar cosmos on the other—a position in which he is able in some measure, at least, to study and interpret both ?

Since the time to which we referred at the beginning of this lecture, when man's dwelling-place was looked at as the centre of a creation which was solely subservient to *his* wants, there has been a reaction to the opposite extreme, and we have heard much of the utter insignificance of the earth in a universe among whose immensities all human belongings are but as a drop in the ocean. When now, however, we learn from Sir William Thomson that the drop of water in our comparison is itself a universe, consisting of units so small that, were the drop magnified to the size of the earth, these units would not exceed in magnitude a cricket-ball,[1] and when, on studying chemistry, we still further learn that these units are not single masses but systems of atoms, we may leave the illusions of the imagination from the one side to correct those from the other, and all will teach us the great lesson that man's place in Nature is not to be estimated by relations of magnitude, but by the intelligence which makes the whole creation his own.

But, if it is man's privilege to follow both the atoms and the stars in their courses, he finds that while thus exercising the highest attributes of his nature he is ever in the presence of an immeasurably superior intelligence, before which he must bow and adore, and thus come to him both the assurance and the pledge of a kinship in which his only real glory can be found.

[1] *Nature*, No. 22, March 31, 1870.

MEMOIR

OF

THOMAS GRAHAM,

BY

PROFESSOR J. P. COOKE.

MEMOIR OF THOMAS GRAHAM.

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It would be difficult to find in the history of science a character more simple, more noble, or more symmetrical in all its parts than that of Thomas Graham, and he will always be remembered as one of the most eminent of those great students of nature, who have rendered our Saxon race illustrious. He was born of Scotch parents in Glasgow in the year 1805, and in that city, where he received his education, all his early life was passed. In 1837 he went to London as Professor of Chemistry in the newly established London University now called University College, and he occupied this chair until the year 1855, when he succeeded Sir John Herschel as Master of the Royal Mint, a post which he held to the close of his life. His death, on the 16th of September last, at the age of sixty, was caused by no active disease, but was simply the wearing out of a constitution enfeebled in youth by privations voluntarily and courageously encountered that he might devote his life to scientific study. As with all earnest students, that life was uneventful, if judged by ordinary standards; and the records of his discoveries form the only materials for his biography. Although one of the most successful investigators of Physical Science, the late Master of the Mint had not that felicity of language or that copiousness of illustration, which added so much to the popular reputation of his dis-

tinguished contemporary, Faraday; but his influence on the progress of science was not less marked or less important. Both of these eminent men were for a long period of years best known to the English public as teachers of Chemistry, but their investigations were chiefly limited to physical problems; yet, although both cultivated the border ground between Chemistry and Physics, they followed wholly different lines of research. While Faraday was so successfully developing the principles of electrical action, Graham with equal success was investigating the laws of molecular motion. Each followed with wonderful constancy, as well as skill, a single line of study from first to last, and to this concentration of power their great discoveries are largely due.

One of the earliest and most important of Graham's investigations, and the one which gave the direction to his subsequent course of study, was that on the diffusion of gases. It had already been recognized that impenetrability in its ordinary sense is not, as was formerly supposed, a universal quality of matter. Dalton had not only recognized that aëriform bodies exhibit a positive tendency to mix, or to penetrate through each other, even in opposition to the force of gravity, but had made this quality of gases the subject of experimental investigation. He inferred, as the result of his inquiry, "that different gases afford no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum; at least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the channel of a stream oppose to the flow of running water." But although this theory of Dalton was essentially correct and involved the whole truth, yet it was supported by no sufficient evidence, and he failed to perceive the simple law which underlies this whole class of phenomena.

Graham, "on entering on this inquiry, found that gases diffuse into the atmosphere with different degrees of ease and rapidity." This was first observed by allowing each gas to diffuse from a bottle into the air through a narrow tube in opposition to the solicitation of gravity. Afterwards an observation of Doebereiner on the escape of hydrogen gas by a fissure or crack in a glass receiver caused him to vary the conditions of his experiments, and led to the invention of the well-known "Diffusion Tube." In this simple apparatus a thin septum of plaster of Paris is used to separate the diffusing gases, which, while it arrests in a great measure all direct currents between the two media,

does not interfere with the molecular motion. Much later, Graham found in prepared graphite a material far better adapted to this purpose than the plaster, and he used septa of this mineral to confirm his early results, in answer to certain ill-considered criticisms in Bunsen's work on Gasometry. These septa he was in the habit of calling his "atomic filters." By means of the diffusion tube Graham was able to measure accurately the relative times of diffusion of different gases, and he found that *equal volumes of any two gases interpenetrate each other in times which are inversely proportional to the square roots of their respective densities*, and this fundamental law was the greatest discovery of our late Foreign Associate. It is now universally recognized as one of the few great cardinal principles which form the basis of Physical Science.

It can be shown, on the principles of pneumatics, that gases should rush into a vacuum with velocities corresponding to the numbers which have been found to express their diffusion times; and, in a series of experiments on what he calls the "*Effusion*" of gases, Graham confirmed by trial this deduction of theory. In these experiments a measured volume of the gas was allowed to find its way into the vacuous jar through a minute aperture in a thin metallic plate, and he carefully distinguished between this class of phenomena and the flowing of gases through capillary tubes into a vacuum, in which case, however short the tube, the effects of friction materially modify the result. This last class of phenomena Graham likewise investigated, and designated by the term "Transpiration."

While, however, it thus appears that the results of Graham's investigation were in strict accordance with Dalton's theory, it must also be evident that Graham was the first to observe the exact numerical relation which obtains in this class of phenomena, and that all-important circumstance entitles him to be regarded as the discoverer of the law of Diffusion. The law, however, as first enunciated, was purely empirical, and Graham himself says that something more must be assumed than that gases are vacua to each other, in order to explain all the phenomena observed; and according to his original view this representation of the process was only a convenient mode of expressing the final result. Such has proved to be the case.

Like other great men, Graham built better than he knew. In the progress of Physical Science during the last twenty-five years, two principles have become more and more conspicuous, until at last they

have completely revolutionized the philosophy of Chemistry. In the first place it has appeared that a host of chemical as well as of physical facts are co-ordinated by the assumption that all substances in the state of gas have the same molecular volume, or, in other words, contain the same number of molecules in a given space; and in the second place, it has become evident that the phenomena of heat are simply the manifestations of molecular motion. According to this view, the temperature of a body is the *vis viva* of its molecules; and since all molecules at a given temperature have the same *vis viva*, it follows that the molecules must move with velocities which are inversely proportional to the square roots of the molecular weights. Moreover, since the molecular volumes are equal, and the molecular weights therefore proportional to the densities of the aëriform bodies in which the molecules are the active units, it also follows that the velocities of the molecules in any two gases are inversely proportional to the square roots of their respective densities. Thus the simple numerical relations first observed in the phenomena of diffusion are the direct result of molecular motion, and it is now seen that Graham's empirical law is included under the fundamental laws of motion. Thus Graham's investigation has become the basis of the new science of molecular mechanics, and his measurements of the rates of diffusion prove to be the measures of molecular velocities.

From the study of diffusion Graham passed by a natural transition to the investigation of a class of phenomena which, although closely allied to the first, as to the effects produced, differ wholly in their essential nature. Here also he followed in the footsteps of Dalton. This distinguished chemist had noticed that a bubble of air separated by a film of water from an atmosphere of carbonic anhydride gradually expanded until it burst. In like manner a moist bladder, half filled with air and tied, if suspended in an atmosphere of the same material, becomes in time greatly distended by the insinuation of this gas through its substance. This effect cannot be the result of simple diffusion, for it is to be remembered that the thinnest film of water, or of any liquid, is absolutely impermeable to a gas as such, and, moreover, only the carbonic anhydride passes through the film, very little or none of the air escaping outward. The result depends, first, upon the solution of the carbonic anhydride by the water on one surface of the film; secondly, on the evaporation into the air, from the other surface, of the gas thus absorbed. Similar ex-

periments were made by Drs. Mitchell and Faust, and others, in which gases passed through a film of india-rubber, entering into a partial combination with the material on one surface, and escaping from it on the other.

Graham not only considerably extended our knowledge of this class of phenomena, but also gave us a satisfactory explanation of the mode in which these remarkable results are produced. He recognized in these cases the action of a feeble chemical force, insufficient to produce a definite compound, but still capable of determining a more or less perfect union, as in the case of simple solution. He also distinguished the influence of mass in causing the formation or decomposition of such weak chemical compounds. The conditions of the phenomena under consideration are simply these: —

First. A material for the septum capable of forming a feeble chemical union with the gas to be transferred.

Secondly. An excess of the gas on one side of the film and a deficiency on the other.

Thirdly. Such a temperature that the unstable compound may orm at the surface, where the aëriform constituent is present in large mass, while it decomposes at the opposite surface, where the quantity is less abundant.

One of the most remarkable results of Graham's study of this peculiar mode of transfer of aëriform matter through the very substance of solid bodies was an ingenious method of separating the oxygen from the atmosphere. The apparatus consisted simply of a bag of india-rubber kept distended by an interior framework, while it was exhausted by a Sprengel pump. Under these circumstances the selective affinity of the caoutchouc determines such a difference in the rate of transfer of the two constituents of the atmosphere that the amount of oxygen in the transpired air rises to forty per cent, and by repeating the process nearly pure oxygen may be obtained. It was at first hoped that this method might find a valuable application in the arts, but in this Graham was disappointed; for the same result has since been effected by purely chemical methods, which are both cheaper and more rapid.

These experiments on india-rubber naturally led to the study of similar effects produced with metallic septa, which, although to some extent previously observed in passing gases through heated metallic tubes, had been only imperfectly understood. Thus, when a stream of

hydrogen or carbonic oxide is passed through a red-hot iron tube, a no inconsiderable portion of the gas escapes through the walls. The same is true to a still greater degree when hydrogen is passed through a red-hot tube of platinum, and Graham showed that through the walls of a tube of palladium hydrogen gas passes, under the same conditions, almost as rapidly as water through a sieve. Moreover, our distinguished Associate proved that this rapid transfer of gas through these dense metallic septa was due, as in the case of the india-rubber, to an actual chemical combination of its material with the metal, formed at the surface, where the gas is in excess, and as rapidly decomposed on the opposite face of the septum. He not only recognized as belonging to this class of phenomena the very great absorption of hydrogen by platinum plate and sponge in the familiar experiment of the Doebereiner lamp, but also showed that this gas is a definite constituent of meteoric iron, — a fact of great interest from its bearing on the meteoric theory.

We are thus led to Graham's last important discovery, which was the justification of the theory we have been considering, and the crowning of this long line of investigation. As may be anticipated from what has been said, the most marked example of that order of chemical compounds, to which the metallic transpiration of aëriform matter we have been considering is due, is the compound of palladium with hydrogen. Graham showed that when a plate of this metal is made the negative pole in the electrolysis of water, it absorbs nearly one thousand times its volume of hydrogen gas, — a quantity approximatively equivalent to one atom of hydrogen to each atom of palladium. He further showed that the metal thus becomes so profoundly altered as to indicate that the product of this union is a definite compound. Not only is the volume of the metal increased, but its tenacity and conducting power for electricity are diminished, and it acquires a slight susceptibility to magnetism, which the pure metal does not possess. The chemical qualities of this product are also remarkable. It precipitates mercury from a solution of its chloride, and in general acts as a strong reducing agent. Exposed to the action of chlorine, bromine, or iodine, the hydrogen leaves the palladium and enters into direct union with these elements. Moreover, although the compound is readily decomposed by heat, the gas cannot be expelled from the metal by simple mechanical means.

These facts recall the similar relations frequently observed between the qualities of an alloy and those of the constituent metals, and suggest the inference made by Graham, that palladium charged with hydrogen

is a compound of the same class, — a conclusion which harmonizes with the theory long held by many chemists, that hydrogen gas is the vapor of a very volatile metal. This element, however, when combined with palladium, is in a peculiarly active state, which sustains somewhat the same relation to the familiar gas that ozone bears to ordinary oxygen. Hence Graham distinguished this condition of hydrogen by the term "Hydrogenium." Shortly before his death a medal was struck at the Royal Mint from the hydrogen palladium alloy in honor of its discovery; but although this discovery attracted public attention chiefly on account of the singular chemical relations of hydrogen, which it brought so prominently to notice, it will be remembered in the history of science rather as the beautiful termination of a life-long investigation, of which the medal was the appropriate seal.

Simultaneously with the experiments on *gases*, whose results we have endeavored to present in the preceding pages, Graham carried forward a parallel line of investigation of an allied class of phenomena, which may be regarded as the manifestations of molecular motion in *liquid* bodies. The phenomena of diffusion reappear in liquids, and Graham carefully observed the times in which equal weights of various salts dissolved in water diffused from an open-mouth bottle into a large volume of pure water, in which the bottle was immersed. He was not, however, able to correlate the results of these experiments by such a simple law as that which obtains with gases. It appeared, nevertheless, that the rate of diffusion differs very greatly for the different soluble salts, having some relation to the chemical composition of the salt which he was unable to discover. But he found it possible to divide the salts into groups of equi-diffusive substances, and he showed that the rates of diffusion of the several groups bear to one another simple numerical ratios.

More important results were obtained from the study of a class of phenomena corresponding to the transpiration of gases through india-rubber or metallic septa. These phenomena, as manifested in the transfer of liquids and of salts in solution through bladder, or a similar membrane, had previously been frequently studied under the names of exosmose and endosmose, but to Graham we owe the first satisfactory explanation. As in the case of gases, he referred these effects to the influence of chemical force, combination taking place on one surface of the membrane, and the compound breaking up on the other, the difference depending, as in the previous instance, on the influence of mass.

He also swept away the arbitrary distinctions made by previous experimenters, showed that this whole class of phenomena are essentially similar, and called this manifestation of power simply "osmose."

While studying osmotic action, Graham was led to one of his most important generalizations, — the recognition of the crystalline and amorphous states as fundamental distinctions in chemistry. Bodies in the first state he called crystalloids; those in the last state, colloids (resembling glue). That there is a difference in structure between crystalloids, like sugar or felspar, and colloids, like barley candy or glass, has of course always been evident to the most superficial observer; but Graham was the first to recognize in these external differences two fundamentally distinct conditions of matter not peculiar to certain substances, but underlying all chemical differences, and appearing to a greater or less degree in every substance. He showed that the power of diffusion through liquids depends very much on these fundamental differences of condition, — sugar, one of the least diffusible of the crystalloids, diffusing fourteen times more rapidly than caromel, the corresponding colloid. He also showed that, in accordance with the general chemical rule, while colloids readily combine with crystalloids, bodies in the same condition manifest little or no tendency to chemical union. Hence in osmose, where the membranes employed are invariably colloidal, the osmotic action is confined almost entirely to crystalloids, since they alone are capable of entering into that combination with the material of the septum on which the whole action depends.

On the above principles Graham based a simple method of separating crystalloids from colloids, which he calls "dialysis," and which was a most valuable addition to the means of chemical analysis. A shallow tray, prepared by stretching parchment paper (an insoluble colloid) over a gutta-percha hoop, is the only apparatus required. The solution to be "dialyzed" is poured into this tray, which is then floated on pure water, whose volume should be eight or ten times greater than that of the solution. Under these conditions the crystalloids will diffuse through the porous septum into the water, leaving the colloids on the tray, and in the course of a few days a more or less complete separation of the two classes of bodies will have taken place. In this way arsenious acid and similar crystalloids may be separated from the colloidal materials with which, in the case of poisoning, they are usually found mixed in the animal juices or tissues.

But besides having these practical applications, the method of dialysis in the hands of Graham yielded the most startling results, developing an almost entirely new class of bodies as the colloidal forms of our most familiar substances, and justifying the conclusion that the colloidal as well as the crystalline condition is an almost universal attribute of matter. Thus, he was able to obtain solutions in water of the colloidal states of aluminic, feoric, chromic, stannic, metastannic, titanic, molybdic, tungstic, and silicic hydrates, all of which gelatinize under definite conditions like a solution of glue. The wonderful nature of these facts can be thoroughly appreciated only by those familiar with the subject, but all may understand the surprise with which the chemist saw such hard, insoluble bodies as flint dissolved abundantly in water and converted into soft jellies. These facts are, without doubt, the most important contributions of Dr. Graham to pure chemistry.

In this sketch of the scientific career of our late Associate, we have followed the logical, rather than the chronological, order of events, hoping thus to render the relations of the different parts of his work more intelligible. It must be remembered, however, that the two lines of investigation we have distinguished were in fact interwoven, and that the beautiful harmony which his completed life presents was the result, not of a preconceived plan, but of a constant devotion to truth, and a childlike faith, which unhesitatingly pressed forward whenever nature pointed out the way.

Although the investigations of the phenomena connected with the molecular motion in gases and liquids were by far the most important of Dr. Graham's labors, he also contributed to chemistry many researches which cannot be included under this head. Of these, which we may regard as his detached efforts, the most important was his investigation of the hydrates and other salts of phosphorus. It is true that the interpretation he gave of the results has been materially modified by the modern chemical philosophy, yet the facts which he established form an important part of the basis on which that philosophy rests. Indeed, it seems as if he almost anticipated the later doctrines of types and polybasic acids, and in none of his work did he show more discriminating observation or acute reasoning. A subsequent investigation on the condition of water in several crystalline salts and in the hydrates of sulphuric acid is equally remarkable. Lastly, Graham also made interesting observations on the combination of alcohol with salts, on the process of etherification, on the slow oxidation of phosphorus,

and on the spontaneous inflammability of phosphuretted hydrogen. It would not, however, be appropriate in this place to do more than enumerate the subjects of these less important studies; and we have therefore only aimed in this sketch to give a general view of the character of the field which this eminent student of nature chiefly cultivated, and to show how abundant was the harvest of truth which we owe to his faithful toil.

Graham was not a voluminous writer. His scientific papers were all very brief, but comprehensive, and his "Elements of Chemistry" was his only large work. This was an admirable exposition of chemical physics, as well as of pure chemistry, and gave a more philosophical account of the theory of the galvanic battery than had previously appeared. Our late Associate was fortunate in receiving during life a generous recognition of the value of his labors. His membership was sought by almost all the chief scientific societies of the world, and he enjoyed to a high degree the confidence and esteem of his associates. Indeed, he was singularly elevated above the petty jealousies and belittling quarrels, which so often mar the beauty of a student's life, while the great loveliness and kindliness of his nature closely endeared him to his friends. He was never married, keeping house with a sister at No. 4 Gordon Square, where he dispensed a liberal hospitality, which has been enjoyed by many of our scientific countrymen who have visited London during the last twenty years.

In concluding, we must not forget to mention that most genial trait of Graham's character, his sympathy with young men, which gave him great influence as a teacher in the College with which he was long associated. There are many now prominent in the scientific world who have found in his encouragement the strongest incentive to perseverance, and in his approval and friendship the best reward of success.

[From the American Journal of Science and Arts, Vol. XIV, Aug., 1877.]

Chemical and Physical Researches; by Thomas Graham. Collected and printed for presentation only. Preface and Analytical Contents, by Dr. R. Angus Smith. Edinburgh, 1876.—What Horace wrote of his own works

"Exegi monumentum ære perennius,"

is equally true of the product of all literary and scientific labor of the highest class, and no more worthy tribute can be paid to intellectual greatness than by carefully cherishing that monument, which the noble intellect during this earthly life erects to itself. Such a recognition, though long delayed, the French Government bestowed both on La Place and on Lavoisier, by publishing magnificent editions of their works. A similar debt of gratitude the American Academy of Arts and Sciences has paid to Rumford; but we do not hesitate to say that the elegant volume before us, in which his two friends,—James Young and R. Angus Smith,—have embodied the "Chemical and Physical Researches of Thomas Graham," is the noblest tribute of all. To the scientific contemporaries of Graham, among whom it has been widely distributed, this volume is the most worthy memorial possible of the successful student of nature whom all honored, and of the man whom all who approached him loved. His modesty of character was in striking contrast with the self-assertion of the Roman poet who could write the famous verse we have quoted above; but no friend of Graham can doubt that this literary tribute would be far more grateful to him than the bronze statue which adorns his native city. Bronze can add no luster to intellectual greatness, and however much it may swell the false glory of the living, to the eyes of posterity it only renders the transient splendor the more vain. Such monuments have their value in so far as by keeping constantly before the people examples of true greatness they serve to educate a nation. But who does not know that the chief motive which erects statues of great men is national vanity, and when will nations learn that they can serve even this selfish aim far more effectually by promoting with pecuniary means the labors of their great scholars while living, and carefully cherishing their works when dead. Every student of science would have preferred that the memorial before us, worthy as it is of one of the noblest scientific scholars which England has produced, should have been a tribute of the nation rather than an offering of two devoted friends, and all must regret that a similar tribute has not been paid to Graham's great contemporary, Michael Faraday.

The great value of memorial volumes like the one which Graham's two friends have presented *gratuitously* to the scientific world is to be found in this,—that they add finish to the com-

pleted work of the great man, they commemorate, and exhibit its unity. The investigations of almost every successful student of nature are directed by a few controlling ideas, and although the parts may seem to his contemporaries to be disconnected, because the results are published at intervals, yet when the work is done, and is seen with the perspective which time gives, the plan appears; and no greater service can be done for the departed scholar than to bring together his scattered papers, and make evident to the world the great thoughts which give unity and dignity to the whole; and not only is the work of his life thus made to appear more worthy, but, what is more important, it is rendered more useful to science.

The trait we have pointed out is most conspicuous in the investigations of Graham, and the service we have commended has been most ably rendered to his deceased friend by Dr. Angus Smith, in the admirable "Preface and Analytical Contents" of the volume we are noticing. It is this feature which in our estimate renders this volume a more worthy memorial than either of the works to which we have referred above. In a biographical notice prepared for the Proceedings of the American Academy of Arts and Sciences, and reprinted in this Journal, III, vol. i, p. 115, we have already expressed our appreciation of the remarkably unique character of Graham's work, and shown that it forms a large part of the experimental basis of the recent science of molecular mechanics; and we are glad to find that our estimate of these investigations has been so fully confirmed. There is but one observation which we desire to add.

Faraday and Graham were two of the most successful discoverers who in any age have illustrated the annals of physical science, and their success was wholly due to the power with which they wielded the inductive method of experimental research. Experiment guided by analogy ever has been, and ever must be, the fundamental condition of all progress in physics, and we regret to see a tendency to undervalue this mode of investigation as compared with the more rigid methods of mathematical deduction. The ability to devise crucial experiments, and to overcome the difficulties which the material conditions of every new physical problem present, is a talent of fully as high an order as that which can marshal differential equations and draw forth the truths which they involve; and this mathematical skill, all important as it is, and essential to the later developments of the science, would be powerless without the data, which experiment has supplied. We would therefore most earnestly commend to the attention of the students of physics, these experimental researches of Graham, as an example of what great results can be attained by purely and very simple experimental means. J. P. C., JR.

Newport, July 9th.

MEMOIR

OF

WILLIAM HALLOWES MILLER.

BY J. P. COOKE.

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MEMOIR OF WILLIAM HALLOWES MILLER.

William Hallowes Miller, who was elected Foreign Honorary Member of this Academy in the place of C. F. Naumann, May 26, 1874, died at his residence in Cambridge, England, on the 20th of May, 1880, at the age of seventy-nine, having been born at Velindre in Wales, April 6, 1801. His life was singularly uneventful even for a scholar. Graduating with mathematical honors at Cambridge in 1826, he became a fellow of his college (St. John's) in 1829, and was elected Professor of Mineralogy in the University in 1832. Amidst the calm and elegant associations of this ancient English university, Miller passed a long and tranquil life, — crowded with useful labors, honored by the respect and love of his associates, and blessed by congenial family ties. This quiet student life was exactly suited to his nature, which shunned the bustle and unrest of our modern world. For relaxation even he loved to seek the retired valleys of the Eastern Alps; and the description which he once gave to the writer, of himself sitting at the side of his wife amidst the grand sceuery, intent on developing crystallographic formulæ while the accomplished artist traced the magnificent outlines of the Dolomite mountains, was a beautiful idyl of science.

Miller's activities, however, were not confined to the University. In 1838 he became a Fellow of the Royal Society, and in 1856 he was appointed its Foreign Secretary, — a post for which he was eminently fitted and which he filled for many years. In 1843 he was selected one of a committee to superintend the construction of the new Parliamentary standards of length and weight, to replace those

which had been lost in the fire which consumed the Houses of Parliament in 1834, and to Professor Miller was confided the construction of the new standard of weight. His work on this important committee, described in an extended paper published in the Philosophical Transactions for 1856, was a model of conscientious investigation and scientific accuracy. Professor Miller was subsequently a member of a new Royal Commission for "examining into and reporting on the state of the secondary standards, and for considering every question which could affect the primary, secondary, and local standards"; and in 1870 he was appointed a member of the "Commission Internationale du Mètre." His services on this commission were of great value, and it has been said that "there was no member whose opinions had greater weight in influencing a decision upon any intricate and delicate question."

Valuable, however, as were Professor Miller's public services on these various commissions, his chief work was at the University. His teacher, Dr. William Whewell, — afterwards the Master of Trinity College, — was his immediate predecessor in the Professorship of Mineralogy at Cambridge. This great scholar, whose encyclopædic mind could not long be confined in so narrow a field, held the professorship only four years, but during this period he devoted himself with his usual enthusiasm to the study of crystallography, and he accomplished a most important work in attracting to the same study young Miller, who brought his mathematical training to its elucidation. It was the privilege of Professor Miller to accomplish a unique work, for the like of which a more advanced science, with its multiplicity of details, will offer few opportunities.

The foundations of crystallography had been laid long before Miller's time. Haüy is usually regarded as the founder of the science; for he first discovered the importance of cleavage, and classed the known facts under a definite system. Taking cleavage as his guide, and assuming that the forms of cleavage were not only the *primitive forms* of crystals as a whole, but also the forms of their *integrant molecules*, he endeavored to show that all secondary forms might be derived from a few primary forms, regarded as elements of nature, by means of *decrements* of molecules at their edges. In like manner he showed that all the forms of a given mineral, like fluor-spar or calcite, might be built up from the integrant molecules by skilfully placing together the primitive forms. Haüy's dissection of crystals, in a man-

ner which appeared to lead to their ultimate crystalline elements, gained for his system great popular attention and applause. The system was developed with great perspicuity and completeness in a work remarkable for the vivacity of its style and the felicity of its illustration. Moreover, a simple mathematical expression was given to the system, and the notation which Haüy invented to express the relation of the secondary to the primary forms, as modified and improved by Lèvy, is still used by the French mineralogists.

The system of Haüy, however, was highly artificial, and only prepared the way for a simpler and more general expression of the facts. The German crystallographer, Weiss, seems to be the first to have recognized the truth that the decrements of Haüy were merely a mechanical mode of representing the fact that all the secondary faces of a crystal make intercepts on the edges of the primitive form which are simple multiples of each other; and this general conception, once gained, it was soon seen that these ratios could be as simply measured on the axes of symmetry of the crystal as on the edges of the fundamental forms; and, moreover, that when crystal forms are viewed in their relation to these axes a more general law becomes evident, and the artificial distinction between primary and secondary forms disappears.

Thus became slowly evolved the conception of a crystal as a group of similar planes symmetrically disposed around certain definite and obvious systems of axes, and so placed that the intercepts, or parameters, on these axes bore to each other a simple numerical ratio. Representing by $a : b : c$ the ratio of the intercepts of a plane on the three axes of a crystal of a given substance, then the intercepts of every other plane of this, or of any other crystal of the same substance, conform to the general proportion $m\,a : n\,b : p\,c$, in which m, n, p are three simple whole numbers. This simple notation, devised by Weiss, expressed the fundamental law of crystallography, and the conception of a crystal as a system of planes, symmetrically distributed according to this law, was a great advance beyond the decrements of Haüy, an advance not unlike that of astronomy from the system of vortices to the law of gravitation. Yet, as the mechanism of vortices was a natural prelude to the law of Newton, so the decrements of Haüy prepared the way for the wider views of the German crystallographers.

Whether Weiss or Mohs contributed most to advance crystallography to its more philosophical stage, it is not important here to inquire. Each of these eminent scholars did an important work in

developing and diffusing the larger ideas, and in showing by their investigations that the facts of nature corresponded to the new conceptions. But to Carl Friedrich Naumann, Professor at the time in the "Bergakademie zu Freiberg," belongs the merit of first developing a complete system of theoretical crystallography based on the laws of symmetry and axial ratios. His "Lehrbuch der reinen und angewandten Krystallographie," published in two volumes at Leipzig in 1830, was a remarkable production, and seemed to grasp the whole theory of the external forms of crystals. Naumann used the obvious and direct methods of analytical geometry to express the quantitative relations between the parts of a crystal; and although his methods are often unnecessarily prolix and his notation awkward, his formulæ are well adapted to calculation, and easily intelligible to persons moderately disciplined in mathematics.

But, however comprehensive and perfect in its details, the system of Naumann was cumbrous, and lacked elegance of mathematical form. This arose chiefly from the fact that the old methods of analytical geometry were unsuited to the problems of crystallography; but it resulted also from a habit of the German mind to dwell on details and give importance to systems of classification. To Naumann the six crystalline systems were as much realities of nature as were the forms of the integrant molecules to Haüy, and he failed to grasp the larger thought which includes all partial systems in one comprehensive plan.

Our late colleague, Professor Miller, on the other hand, had that power of mathematical generalization which enabled him to properly subordinate the parts to the whole, and to develop a system of mathematical crystallography of such simplicity and beauty of form that it leaves little to be desired. This was the great work of his life, and a work worthy of the University which had produced the "Principia." It was published in 1839, under the title "A Treatise on Crystallography;" and in 1863, the substance of the work was reproduced in a more perfect form, still more condensed and generalized, in a thin volume of only eighty-six pages, which the author modestly called "A Tract on Crystallography."

Miller began his study of crystallography with the same materials as Naumann; but, in addition, he adopted the beautiful method of Franz Ernst Neumann of referring the faces of a crystal to the surface of a circumscribed sphere by means of radii drawn perpendic-

ular to the faces. The points where the radii meet the spherical surface are the poles of the faces, and the arcs of great circles connecting these poles may obviously be used as a measure of the angles between the crystal faces. This invention of Neumann's was the germ of Miller's system of crystallography; for it enabled the English mathematician to apply the elegant and compendious methods of spherical trigonometry to the solution of crystallographic problems; and Professor Miller always expressed his great indebtedness to Neumann not only for this simple mode of defining the position of the faces of a crystal, but also for his method of representing the relative position of the poles of the faces on a plane surface by a beautiful application of the methods of stereographic and gnomonic projection. This method of representing a crystal shows very clearly the relations of the parts, and was undoubtedly of great aid to Miller in assisting him to generalize his deductions.

From the outset, Professor Miller apprehended more clearly than any previous writer the all-embracing scope of the great law of crystallography. He opens his Treatise with its enunciation, and from this law as the fundamental principle of the subject the whole of his system of crystallography is logically developed. Beyond this, all that is peculiar to Miller's system is involved in two or three general theorems. The rest of his Treatise consists of deductions from these principles and their application to particular cases.

One of the most important of these principles, and one which in the Treatise is involved in the enunciation of the fundamental law of crystallography, is in its essence nothing but an analytical device. As we have already stated, Weiss had shown that, if $a : b : c$ represent the ratio of the intercepts of any plane of a crystal on the three axes x, y, and z respectively, the intercepts of any other possible plane must satisfy the proportion —

$$A : B : C = ma : nb : pc$$

in which m, n, and p are simple whole numbers. The irrational values a, b, and c are fundamental magnitudes for every crystalline substance;* and Miller called these relative magnitudes the parameters

* For example, the native crystals of sulphur have $a : b : c = 1 : 2.340 : 1.238$,
Crystals of gypsum have $a : b : c = 1 : 0.413 : 0.691$,
Crystals of tin stone have $a : b : c = 1 : 1 : 0.6724$,
And crystals of common salt have $a : b : c = 1 : 1 : 1$.

of the crystals, while he called the whole numbers, m, n, and p, the indices of the respective planes. But, instead of writing the proportion which expresses the law of crystallography as above, he gave to it a slightly different form, thus, —

$$A : B : C = \frac{1}{h}\, a : \frac{1}{k}\, b : \frac{1}{l}\, c,$$

and used in his system for the indices of a plane the values $h : k : l$, which are also in the ratio of whole numbers, and usually of simpler whole numbers than $m : n : p$. This seems a small difference; for $h\ k\ l$ in the last proportion are obviously the reciprocals of $m\ n\ p$ in the first; but the difference, small as it is, causes a wonderful simplification of the formulæ which express the relations between the parts of a crystal. From the last proportion we derive at once

$$\frac{1}{h} \cdot \frac{a}{A} = \frac{1}{k} \cdot \frac{b}{B} = \frac{1}{l}\, \frac{c}{C}$$

which is the form in which Miller stated his fundamental law.

If P represents the "pole" of a face whose "indices" are $h\,k\,l$, that is, represents the point where the radius drawn normal to the face meets the surface of the sphere circumscribed around the crystal (the sphere of projection, as it is called), and if X, Y, Z represent the points where the axes of the crystal meet the same spherical surface,* then it is evident that $X\,Y$, $X\,Z$, and $Y\,Z$ are the arcs of great circles, which measure the inclination of the axes to each other, and that $P\,X$, $P\,Y$, and $P\,Z$ are arcs of other great circles, which measure the inclination of the plane $(h\,k\,l)$ on planes normal to the respective axes; and, also, that these several arcs form the sides of spherical triangles thus drawn on the sphere of projection. Now, it is very easily shown that

$$\frac{a}{h} \cos\, PX = \frac{b}{k} \cos\, PY = \frac{c}{l} \cos\, PZ$$

and by means of this theorem we are able to reduce a great many problems of crystallography to the solution of spherical triangles.

Another very large class of problems in crystallography is based on the relation of faces in a zone; that is of faces which are all parallel to one line called the zone axis, and whose mutual intersections, therefore, are all parallel to each other. If now $h\ k\ l$ and $p\ q\ r$ are the indices

* The origin of the axes is always taken as the centre of the sphere of projection.

of any two planes of a zone (not parallel to each other) any other plane in the same zone must fulfil the condition expressed by the simple equation

$$\mathrm{u}\,u + \mathrm{v}\,v + \mathrm{w}\,w = o$$

where u v and w are the indices of the third plane and u v w have the values

$$\mathrm{u} = k\,r - l\,q \quad \mathrm{v} = l\,p - h\,r \quad \mathrm{w} = h\,q - k\,p$$

Since h k l and p q r are whole numbers, it is evident that u v w must also be whole numbers and these quantities are called the indices of the zone. The three whole numbers which are the indices of a plane when written in succession serve as a very convenient symbol of that plane, and represent to the crystallographer all its relations; and in like manner Miller used the indices of a zone enclosed in brackets as the symbol of that zone. Thus 123, 531, 010 are symbols of planes, and [111], [213], [001] symbols of zones.

An additional theorem enables us to calculate the symbols of a fourth plane in a zone when the angular distances between the four planes and the symbols of three of them are known, but this problem cannot be made intelligible with a few words.

The few propositions to which we have referred involve all that is essential and peculiar to the system of Professor Miller. These given, and the rest could be at once developed by any scholar who was familiar with the facts of crystallography; and the circumstance that its essential features can be so briefly stated is sufficient to show how exceedingly simple the system is. At the same time, it is wonderfully comprehensive, and the student who has mastered it feels that it presents to him in one grand view the entire scheme of crystal forms, and that it greatly helps him to comprehend the scheme as a whole, and not simply as the sum of certain distinct parts. So felt Professor Miller himself; and, while he regarded the six systems of crystals of the German crystallographers as natural divisions of the field, he considered that they were bounded by artificial lines which have no deeper significance than the boundary lines on a map. How great the unfolding of the science from Haüy to Miller, and yet now we can see the great fundamental ideas shining through the obscurity from the first. What we now call the parameters of a crystal were to Haüy the fundamental dimensions of his "integrant molecules," our indices were his "decrements," and our conceptions of symmetry his "fundamental

forms?" There has been nothing peculiar, however, in the growth of crystallography. This growth has followed the usual order of science, and here as elsewhere the early, gross, material conceptions have been the stepping-stones by which men rose to higher things. In sciences like chemistry, which are obviously still in the earlier stages of their development, it would be well if students would bear in mind this truth of history, and not attach undue importance to structural formulæ and similar mechanical devices, which, although useful for aiding the memory, are simply hinderances to progress as soon as the necessity of such assistance is passed. And when the life of a great master of science has ended, it is well to look back over the road he has travelled and while we take courage in his success consider well the lesson which his experience has to teach; and, as progress in this world's knowledge has ever been from the gross to the spiritual, may we not rejoice as those who have a great hope?

Although the exceeding merit of the "Treatise on Crystallography" casts into the shade all that was subordinate, we must not omit to mention that Professor Miller published an early work on Hydrostatics, and numerous shorter papers on Mineralogy and Physics, which were all valuable, and constantly contained important additions to knowledge. Moreover, the "New Edition of Phillips's Mineralogy" which he published in 1852 in connection with H. J. Brooke owed its chief value to a mass of crystallographic observations which he had made with his usual accuracy and patience during many years, and there tabulated in his concise manner. As has been said by one of his associates in the Royal Society, "it is a monument to Miller's name, although he almost expunged that name from it."* It is due to Professor Miller's memory that his works should be collated, and especially that by a suitable commentary his "Tract on Crystallography" should be made accessible to the great body of the students of physical science, who have not, as a rule, the ability or training which enables them to apprehend a generalization when solely expressed in mathematical terms. The very merits of Professor Miller's book as a scientific work renders it very difficult to the average student, although it only involves the simplest forms of algebra and trigonometry.

Independence, breadth, accuracy, simplicity, humility, courtesy, are luminous words which express the character of Professor Miller. In

* Obituary Notices from the Proceedings of the Royal Society, No. 206, 1880, to which the writer has been indebted for several biographical details.

his genial presence the young student felt encouraged to express his immature thoughts, which were sure to be treated with consideration, while from a wealth of knowledge the great master made the error evident by making the truth resplendent. It was the greatest satisfaction to the inexperienced investigator when his observations had been confirmed by Professor Miller, and he was never made to feel discouraged when his mistakes were corrected. The writer of this notice regards it as one of the great privileges of his youth, and one of the most important elements of his education, to have been the recipient of the courtesies and counsel of three great English men of science, who have always been "his own ideal knights," and these noble knights were Faraday, Graham, and Miller.

SKETCH OF PROFESSOR J. P. COOKE, Jr.

[Reprinted from The Popular Science Monthly, February, 1877.]

The position occupied by this gentleman in American science is one of marked distinction as a successful original investigator, and also as an efficient reformer in the work of scientific education. He is known at home and abroad both by the extent and importance of his experimental researches, and by the high-toned and thorough-going character of his expository works on chemistry and physics. It is a fact of no little significance that, although Prof. Cooke had the advantage of a university training, he was self-taught in chemistry, as his collegiate culture afforded no special preparation for his chosen field of labor, while the impulse which started him in a scientific career came from popular lectures outside the university. Yet he has probably done more than any other man to give chemical science its proper status in the collegiate curriculum as a valuable disciplinary study entitled to a leading place in an effective system of liberal culture.

Josiah Parsons Cooke, Jr., was born in Boston, October 12, 1827, and is a descendant of Major Aaron Cooke, who emigrated from England in 1630, and became one of the first settlers of Dorchester, and afterward of Northampton, Massachusetts. His father, a lawyer, is still living, at the advanced age of ninety, the oldest member of the Suffolk Bar.

Young Cooke received his early education at the Boston Latin School, and entered Harvard College in 1844, where he graduated in 1848. After passing a year in Europe for the recovery of his health, he returned to the university in 1849, as Tutor in Mathematics. He was soon afterward appointed Instructor in Chemistry, and at the

close of the following year he succeeded to the Erving Professorship of Chemistry and Mineralogy, which he has held ever since.

Prof. Cooke never had the advantages of a European education, or indeed of any systematic teaching in science. He acquired his taste for chemistry at the early lectures of the Lowell Institute, in Boston, given by the elder Silliman, and, with the apparatus he had collected in a little laboratory in his father's house while a boy, he began his first course of lectures at Cambridge. For several years preceding his appointment no regular instruction in chemistry had been given to the undergraduates, and he had, therefore, the whole labor of developing this department of the college from the beginning. Although scientific schools had been previously established, both at Cambridge and at New Haven, yet Prof. Cooke was probably the first to introduce into our American colleges the experimental method of teaching physical science. He was, at first, greatly hampered by the inflexible recitation system, then universal, and success was only gained after many trials; but Harvard College may now claim to offer its undergraduates as broad and thorough instruction in the various departments of chemistry, including mineralogy, as any similiar institution in the world. Like most American men of science, Prof. Cooke's first duty was to teach, and his time and energy have accordingly been chiefly spent in developing methods of science-teaching, in building laboratories, in making collections, and in providing the various means of scientific instruction.

In connection with his teaching Prof. Cooke has published the following books:

"Chemical Problems and Reactions, to accompany Stöckhardt's Elements of Chemistry," in 1857; "Elements of Chemical Physics," in 1860; "Principles of Chemical Philosophy," in 1869.

In a notice of the last book the London *Chemical News* says: "So far as our recollection goes, we do not think that there exists in any language a book on so difficult a subject as this, so carefully, clearly, and lucidly written;" and in noticing the same book the *American Journal of Science* says: "To Prof. Cooke, more than to any American, is due the credit of having made chemistry an exact and disciplinary study in our colleges."

Prof. Cooke has given many courses of popular lectures in different cities—Lowell, Worcester, Brooklyn, Baltimore, and Washington—besides five courses at the Lowell Institute in Boston. His course of lectures at the Brooklyn Institute, in 1860, was subsequently published under the title of "Religion and Chemistry; or, Proofs of God's Plan in the Atmosphere and its Elements" (1864). In these discourses he aimed to show that the argument for design is not invalidated by the theories of evolution.

A course of lectures on electricity at the Lowell Institute, Boston,

in the winter of 1868–'69, was followed by the publication, in the *Journal of the Franklin Institute*, of a series of papers on the "Absolute System of Electrical Measurements" and on the "Theory of the Voltaic Battery." In the last he developed a new theory of electricity, which has also been embodied in the later editions of his "Chemical Philosophy." This theory, like that of Dufay, admits two electrical fluids; but it regards these as separable constituents of the ether of space. These ethereal fluids, more or less blended, form an atmosphere around every molecule held in place by the immense force of molecular attraction; and when, by the various causes of electrical disturbance, the electrical ethers become more or less isolated on the same or on different molecules, the two tend to flow together with great rapidity in virtue of their wonderful elasticity. If we assume that this motion takes place in accordance with the well-known laws of the diffusion of gases, the theory gives a satisfactory explanation of all well-established electrical phenomena.

In the autumn of 1872 Prof. Cooke delivered an interesting and important course of lectures on the "New Chemistry," which was subsequently published in the "International Scientific Series." His volume is one of the best and most successful of these books, and has been very highly appreciated both in this country and abroad, having been translated into most of the languages of Europe.

Among Prof. Cooke's lesser scientific publications may be mentioned the following:

1. "On the Relation between the Atomic Weights of the Chemical Elements" ("Memoirs of the American Academy," vol. v., 1854).

It was first shown in this paper that when the elementary substances are classified in natural groups, their atomic weights and other physical qualities are related by regular differences.

2. "On Two New Crystalline Compounds of Zinc and Antimony, and on the Cause of the Variation of Composition observed in their Crystals" ("Memoirs of the American Academy," vol. v., 1855).

This investigation proved that the crystalline form of these compounds was preserved under very considerable variations of composition, and indicated that the excess of one or the other constituent depended not solely on the composition of the menstruum in which the crystals were formed, but also on the chemical force which determines the union of the elements in definite proportions. The subject was still further discussed in the following paper, published during a visit to England.

3. "Crystalline Form not necessarily an Indication of Definite Chemical Composition, or on the Possible Variations of Composition in a Mineral Species independent of the Phenomena of Isomorphism" (*Philosophical Magazine* for June, 1860).

4. "On the Dimorphism of Arsenic, Antimony, and Zinc" (*American Journal of Science* for March, 1861).

It was here proved that all three of these elements are capable of crystallizing in octahedrons of the regular system.

5. "On Octahedral Galena" (*American Journal of Science* for January, 1863).

In this it was shown that the octahedral cleavage in this singular variety of galena from Lebanon County, Pennsylvania, is merely an unusual development of a constant condition.

6. "Crystallographic Examination of the Hebron Childrenite, and Comparison of this Variety with the Childrenite of Tavistock" (*American Journal of Science* for September, 1863).

7. "Crystallographic Examination of the Acid Tartrates of Cæsia and Rubidia" (*American Journal of Science* for January, 1864).

8. "On the Projection of the Spectra of the Metals" (*American Journal of Science* for September, 1865).

9. "On the Construction of a Spectroscope with a Number of Prisms by which the Angle of Minimum Deviation for any Ray may be accurately measured" (*American Journal of Science* for November, 1865).

10. "On the Heat of Friction" ("Proceedings of the American Academy," 1865).

11. "On the Aqueous Lines of the Solar Spectrum" ("Proceedings of the American Academy," 1866).

By comparing observations with the spectroscope and the hygrometer, it was in this paper first shown that a large part of the air-lines in the solar spectrum are due to aqueous vapor.

12. "On Danalite, a New Mineral Species from the Granite of Rockport, Massachusetts" (*American Journal of Science* for July, 1866).

This is a well-marked species allied to Helvin, but containing zinc in place of manganese.

13. "On Cryophyllite, a New Mineral Species of the Mica Family, with Some Associated Minerals in the Granite of Rockport, Massachusetts" (*American Journal of Science* for March, 1867).

Besides establishing a new species, this paper shows that in the veins of the Rockport granite there are closely associated a unicilicate and a bisilicate mica, which are isomorphous with each other, a circumstance which renders probable the theory that the wide variations in the composition of the micas may result from an isomorphous mixture of two similar types.

14. "On Certain Lecture Experiments, and on a New Form of Endiometer" (*American Journal of Science* for September, 1867).

15. "A Method of determining the Amounts of Protoxide of Iron in Silicates not soluble in the Ordinary Mineral Acids" (*American Journal of Science* for November, 1867).

16. "Crystallographic Determination of Some American Chlorites" (*American Journal of Science* for September, 1867).

The paper gives some new measurements of angles, and shows that there are two crystallographic types of chlorites corresponding to the well-known types of micas. It is further shown that there is a variation of optical angles in the chlorites, even on the same specimens, like that observed with the micas, and the inference is drawn that the variation is due to a similar cause.

17. "Atomic Ratios" (*American Journal of Science* for May, 1869).

It was for the first time pointed out in this paper that what mineralogists have long called the oxygen ratio of a silicate is really the ratio between the atomicities of the acid and basic radicals in these salts.

18. "The Vermiculites—their Crystallographic and Chemical Relations to the Micas, together with a Discussion of the Cause of the Variation of the Optical Angle in these Minerals" ("Proceedings of the American Academy," 1873).

This monograph contains the chemical analyses and crystallographic descriptions of several micaceous minerals which are here classified together, and shows that the variations of the optical angle in the micaceous species is due to the interfoliation of the different members of a macle. It also points out the close relation between hexagonal and trimetric crystals by showing that a hexagonal form and structure may result from a similar macling of trimetric crystals the prismatic angle of which is 120°.

19. "Melanosiderite, a New Mineral Species from Mineral Hill, Delaware County, Pennsylvania" ("Proceedings of the American Academy," 1875).

20. "On Two New Varieties of Vermiculites, with a Revision of Other Members of this Group," published in connection with F. A. Gooch ("Proceedings of the American Academy," 1875).

21. "On a New Mode of manipulating Hydric Sulphide" ("Proceedings of the American Academy," 1876).

This in application of the soda-water fountain, by which hydric sulphide is dissolved in water under pressure, and the magnet readily applied in a concentrated form.

22. "On the Process of Reverse Filtering, and its Application to Large Masses of Material" ("Proceedings of the American Academy," 1876).

This enumeration occupies but a small space; but when it is considered that each paper only states the results of elaborate and protracted original and experimental investigation, where the unverified guesses and the trials that go for nothing do not appear, we can form some idea of the amount of labor involved in the quiet life of a true scientific man.

Prof. Cooke has also written various articles for encyclopædias and reviews, and published several addresses. His discourse on "Sci-

entific Culture," delivered at the opening of the summer courses of instruction in chemistry, at Harvard University, July 7, 1875, printed in THE POPULAR SCIENCE MONTHLY for September, 1875, and republished in London, was one of the ablest contributions to the literature of scientific education that have appeared in a long time. Prof. Cooke's life has been one of valuable scientific service, which has, moreover, met with wide and cordial appreciation. He has been honored by the membership of many learned societies in this country and in Europe, and was quite recently elected foreign honorary member of the Chemical Society of London.